53-2; 3,4-dimethoxyphenylacetic acid, 93-40-3; ethyl 2-nitro-5-methoxyphenylacetate, 117559-88-3; 2-nitro-4,5-dimethoxyphenethyl alcohol, 73357-23-0; 2-nitro-4,5-dimethoxyphenylacetic acid, 73357-18-3; 2-nitro-4,5-dimethoxyphenethyl chloride, 90869-96-8; 2-(2-chloroethyl)-4,5-dimethoxyphenyl isocyanate, 110905-13-0; 3,4-dimethoxyphenethyl fluoride, 117559-89-4; 3,4-dimethoxyphenethyl alcohol, 7417-21-2; 2-(2-fluoroethyl)-4,5-dimethoxynitrobenzene, 117559-90-7; 2-(2-fluoroethyl)-4,5-dimethoxyphenyl isocyanate, 117559-91-8; *p*-aminophenol, 59000-01-0.

Supplementary Material Available: Table of infrared, ^1H NMR, and ^{13}C NMR spectral data for compounds not given in the Experimental Section, preparations of **1c–e**, and the ^1H NMR spectra of **2a**, **2b**, and **3b** (8 pages). Order information is given on any current masthead page.

Stereochemistry in the Michael Addition of Silylcuprate to α,β-Unsaturated Sulfoxide

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Lithium bis(dimethylphenylsilyl)cuprate (**2**), in contrast to dialkylcuprates, reacted with α,β-unsaturated sulfoxides **1** to give Michael products **3** and **4** in good yields. The *E* and *Z* sulfoxides **1** afforded predominantly **3** and **4**, respectively. When the reaction was quenched with deuterium oxide, four α-deuteriated sulfoxides **5–8** were obtained. While the ratio of **5** to **6** was 90:10 from (*E*)-**1** and 70:30 from (*Z*)-**1**, **7** and **8** were formed in equal amounts irrespective of the starting sulfoxides.

α,β-Unsaturated sulfoxides have been utilized in many asymmetric syntheses as Michael acceptors[1] since the pioneering works of Stirling[2] and Ogura.[3] But a problem in this methodology is the difficulty in predicting the stereochemistry of the β-carbon, that is, which diastereomeric face a nucleophile comes from. This problem is complicated particularly in the acyclic sulfoxides because there is no definite information on the conformer to participate in the reaction. The most reliable system studied has been an α-keto α,β-unsaturated sulfoxide reported by Posner,[4] in which metal chelation between the carbonyl and sulfoxide oxygens fixed the conformation and the nucleophile approached from a less crowded face. Recently Hehre[5] reported a theoretical study on the model reaction of methyl vinyl sulfoxide with hydride, suggesting that the nucleophilic attack was anti to the sulfur lone pair and syn to the methyl of the reacting conformer in which S=O was cis and coplanar to the C=C bond. He pointed out simultaneously that this prediction was in accord with the electronic factor but contrary to steric considerations, and not valid in the systems where chelation occurred.

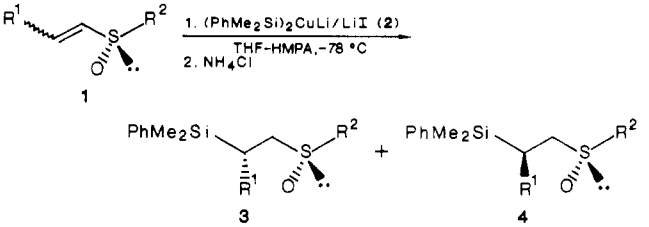
With respect to the stereochemistry of the α-carbon, little has been known in the Michael addition. The only definite example was the α-sulfinylcyclopentenone system,[6] but the direction of electrophilic attack was controlled by the ring. On the other hand, the stereochemistry and reactivity of α-sulfinyl carbanion itself prepared by the proton abstraction from benzylic sulfoxide have been in controversy for a long period, and recently, the original work by Durst was reinvestigated by Ohno.[7] However, the carbanion formed by the Michael addition would be different from that in many respects, particularly because a new chiral center (β-carbon) is adjacent to it.

Insight into this question is disturbed by the limitations of nucleophiles. The sulfoxide having no carbonyl group on the α-position has reacted only with malonic esters[3] and protic substrates such as amines[2] and alcohols.[8] The exceptional example other than this category was the reaction of *p*-chlorophenyl vinyl sulfoxide with dialkylcuprates under special conditions.[9]

In this paper we report a new reaction of α,β-unsaturated sulfoxide with silylcuprate and discuss the stereochemistry of the Michael addition.

Results and Discussion

A reaction of phenyl vinyl sulfoxide (**1a**) with lithium bis(dimethylphenylsilyl)cuprate (**2**)[10] at −78 °C in THF–HMPA[11] followed immediately by quenching with ammonium chloride gave 2-(dimethylphenylsilyl)ethyl phenyl sulfoxide (**3a**) in 70% yield. A longer reaction time caused a decrease of the yield and formation of undefined materials. Similarly, racemic (**1a–d**) and R_s chiral (**1e,f**) α,β-unsaturated sulfoxides reacted with **2** to afford the Michael adducts **3** and **4** in good yields (Table I). The two diastereomers **3** and **4** were easily separated from each other by column chromatography: **4** eluted first.



(1) (a) Posner, G. H. *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic: New York, 1983; Vol. 2, Chapter 8. (b) Mikolajczyk, M.; Drabowicz, J. *Topics in Stereochemistry*; Allinger, N. L., Eliel, E. L., Wilen, S. H., Eds.; Wiley-Interscience: New York, 1982; Vol. 13, p 333.
(2) Abbott, D. J.; Colonna, S.; Stirling, C. J. M. *J. Chem. Soc., Chem. Commun.* **1971**, 471.
(3) Tsuchihashi, G.; Mitamura, S.; Inoue, S.; Ogura, K. *Tetrahedron Lett.* **1973**, 323.
(4) Reference 1a.
(5) Kahn, S. D.; Hehre, W. J. *J. Am. Chem. Soc.* **1986**, *108*, 7399.
(6) Posner, G. H.; Mallamo, J. P.; Miura, K. *Ibid.* **1981**, *103*, 2886.
(7) Nakamura, K.; Higaki, M.; Adachi, S.; Oka, S.; Ohno, A. *J. Org. Chem.* **1987**, *52*, 1414.
(8) Tsuchihashi, G.; Mitamura, S.; Ogura, K. *Tetrahedron Lett.* **1973**, 2469.
(9) Sugihara, H.; Tanikaga, R.; Tanaka, K.; Kaji, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 655.
(10) Ager, D. J.; Fleming, I.; Patel, S. K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2520.
(11) The reaction in the absence of HMPA did not afford **3a**.

0022-3263/89/1954-0058$01.50/0

Table I. Reaction of α,β-Unsaturated Sulfoxide 1 with Lithium Bis(dimethylphenylsilyl)cuprate (2)[a]

entry	sulfoxide[b]	R^1	R^2	product	total yield,[c] %	3:4[d]
1	**1a**	H	Ph	**3a**	70	-
2	(*E*)-**1b**	CH_3	Ph	**3b + 4b**	48	88:12
3	(*Z*)-**1b**	CH_3	Ph	**3b + 4b**	47	6:94
4	(*E*)-**1c**	n-C_5H_{11}	Ph	**3c + 4c**	82	80:20
5	(*Z*)-**1c**	n-C_5H_{11}	Ph	**3c + 4c**	73	25:75
6	(*E*)-**1d**	Ph	Ph	**3d + 4d**	72	79:21
7	(*Z*)-**1d**	Ph	Ph	**3d + 4d**	67	20:80
8	(*E*)-**1e**	n-C_5H_{11}	*p*-Tol	**3e + 4e**	67	75:25
9	(*Z*)-**1e**	n-C_5H_{11}	*p*-Tol	**3e + 4e**	70	20:80
10	(*E*)-**1f**	Ph	*p*-Tol	**3f + 4f**	78	85:15
11	(*Z*)-**1f**	Ph	*p*-Tol	**3f + 4f**	70	23:77

[a] Solvent: THF–HMPA (1.2 equiv). Temperature: −78 °C. Reaction time: immediate quenching (entries 1–5), 5 min (entries 8 and 9), 15 min (entries 6, 7, 10, and 11). [b] Racemic sulfoxides (**1a–d**) and R_s chiral (**1e,f**). [c] Combined isolated yields. [d] Ratios of isolated yields.

Table II. Reaction of Phenyl (*E*)-Styryl Sulfoxide (1d) with (Dimethylphenylsilyl)copper Reagents in Various Solvents[a]

entry	copper reagent	solvent	total yield,[b] %	3d:4d[b]
1	$(PhMe_2Si)_2CuLi/LiI$ (**2**)	THF–hexane (3:1)	69	80:20
2	**2**	THF	61	87:13
3	**2**	THF–HMPA (1.2 equiv)	72	79:21
4	**2**	THF–HMPA (3.0 equiv)	57	87:13
5	**2**	THF–18-crown-6 (1.2 equiv)	68	84:16
6	$(PhMe_2Si)_2CuLi/LiCN$	THF	87	65:35
7	$(PhMe_2Si)_2CuLi/LiBr/SMe_2$	THF	60	81:19
8	$(PhMe_2Si)_2CuLi/LiI/BF_3{\cdot}OEt_2$	THF	no adduct[c]	
9	$(PhMe_2Si)Cu/LiI/BF_3{\cdot}OEt_2$	THF	no adduct[d]	

[a] Conditions: 15 min, −78 °C. [b] Isolated yields and ratios. [c] No sulfoxide **1d** was recovered. 4-(Dimethylphenylsilyl)butanol, an adduct of the cuprate and THF, was isolated in 37% yield. [d] The sulfoxide **1d** was recovered unchanged in 90% yield.

Table III. Deuterium Oxide Quenching of the Reaction of 1d and 1f with 2[a]

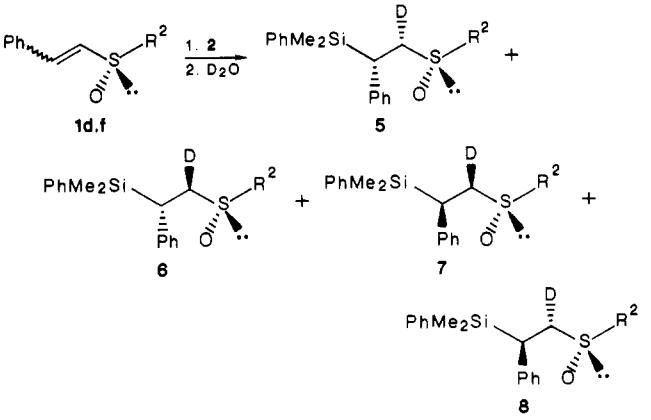
entry	sulfoxide[b]	R^2	total yield,[c] %	(5 + 6):(7 + 8)[c]	5:6[d]	7:8[e]
1	(*E*)-**1d**	Ph	72	79:21	90:10	54:46
2	(*Z*)-**1d**	Ph	67	20:80	73:27	40:60
3	(*E*)-**1f**	*p*-Tol	78	85:15	86:14	55:45
4	(*Z*)-**1f**	*p*-Tol	70	23:77	70:30	54:46

[a] Reaction conditions were identical with those described in Table I. [b] Racemic sulfoxide **1d** and R_s chiral **1f**. [c] Isolated yields and ratios. [d] Determined by ^1H NMR. [e] Determined by ^1H NMR after oxidation to the sulfones **10** and **11**.

Comparing the pair of *E* and *Z* sulfoxides **1**, the total yields are nearly equal but the diastereomer ratios are just opposite. The selectivities for **3** from (*E*)-**1** and **4** from (*Z*)-**1** are about 80:20. This result means that the silylcuprate **2** comes from the same diastereomeric face of probably the same conformer in both cases. It is noteworthy that this reaction, coupled with a ready removal of the sulfinyl group (see Stereochemical Assignment), provides a potentially useful method for the preparation of the optically active C-centered alkylsilanes.[12]

Then the reaction of (*E*)-styryl sulfoxide **1d** with **2** and other (dimethylphenylsilyl)copper reagents was carried out in various solvents (Table II). No drastic solvent effect was observed on the yield and diastereomer ratio as a whole. Of the copper reagents, that derived from copper(I) cyanide gave the best total yield, but the slectivity was severely decreased (entry 6).

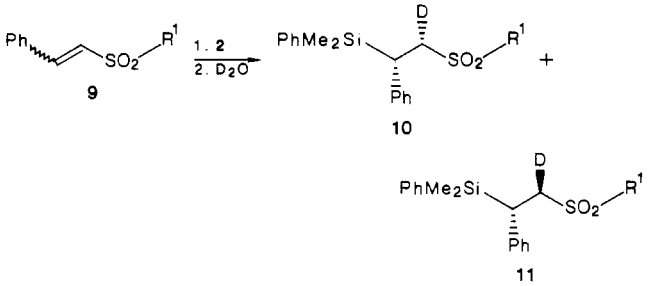
Next we quenched the reaction with deuterium oxide to study the stereochemistry of the α-carbon[13] (Table III). (*E*)- and (*Z*)-Styryl sulfoxides **1d** and **1f** gave a mixture of four diastereomers **5–8**, which was separated into two fractions (**5** + **6** and **7** + **8**, corresponding to **3** and **4**, respectively) by column chromatography. Deuterium was quantitatively incorporated in both fractions (>98%, by ^1H NMR and MS). The total yield and (**5** + **6**):(**7** + **8**) ratio were the same as in previous results. The stereochemistry of the deuteriation shows three levels of selectivities. A good **5**:**6** ratio was observed, starting from *E* sulfoxides (entries 1 and 3), but this ratio was decreased in the reaction of *Z* sulfoxides (entries 2 and 4). In contrast, **7** and **8** were formed in nearly equal amounts irrespective of the starting sulfoxides.



Here, the question is which of two chiral centers (β-carbon and sulfur) controls the stereochemistry described above. According to the literature results on the deuteriation of benzylic sulfoxides in THF,[7] the isomers in which the deuterium was syn to S=O, that is, **5** and **8**, would be preferred to **6** and **7**, respectively. In order to evaluate the effect of the β-carbon, we carried out the reaction of styryl sulfones **9** with the cuprate **2** under identical conditions.

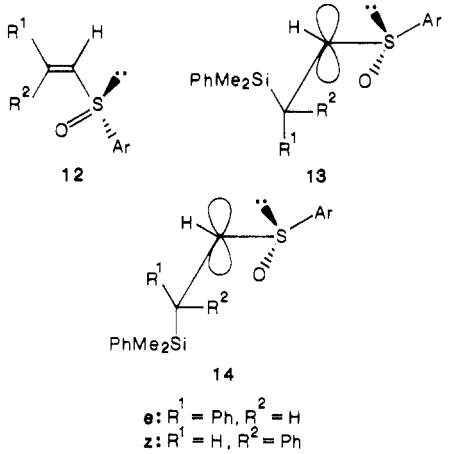
(12) Paquette, L. A.; Gilday, J. P.; Ra, C. S.; Hoppe, M. *J. Org. Chem.* **1988**, *53*, 704.
(13) Quenching with methyl iodide was unsuccessful.

All sulfones **9** gave the Michael adducts **10** and **11**, and the syn products **10** were predominant. This result suggests that, in the reaction of the sulfoxides **1d** and **1f**, formation of the diastereomers **5** and **7** is enriched by the chiral β-carbon.



(*E*)-**9d**: R^1 = Ph 85% (65:35)
(*E*)-**9f**: R^1 = *p*-Tol 85% (69:31)
(*Z*)-**9f**: R^1 = *p*-Tol 90% (65:35)

The overall stereochemistry in this reaction could be rationalized as follows. It seems reasonable for consideration of the stereochemistry on the β-carbon to assume that S=O is cis and coplanar to C=C in the reacting conformer **12** as predicted by the theoretical study.[5] Then the aggregated bulky silylcuprate prefers to attack from the less crowded face, that is, anti to aryl on sulfur to give α-sulfinyl carbanion **13** predominantly (80:20). The minor intermediate **14** may be derived either from **12** by the opposite face attack or from the other conformer in which the sulfur lone pair is cis and coplanar to C=C.

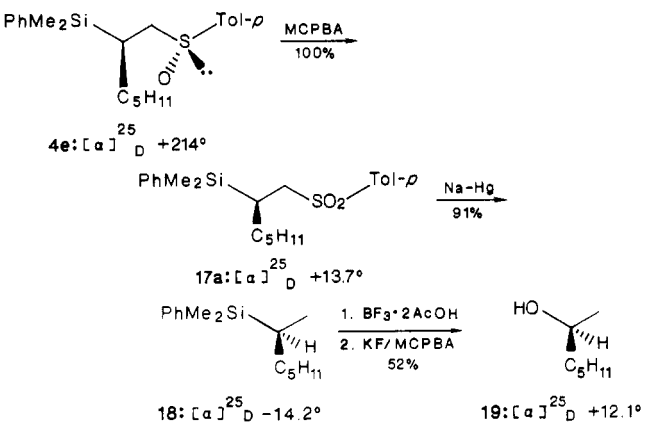


e: R^1 = Ph, R^2 = H
z: R^1 = H, R^2 = Ph

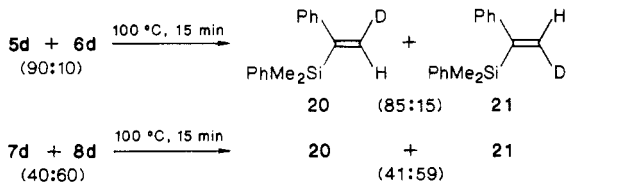
In the reaction of *E* sulfoxides, the stereoelectronic effect of the silyl group[14] matches that of sulfoxide in **13e** and mismatches that in **14e**. Therefore, deuterium comes from the *si* face in **13e** to give **5** selectively (**5**:**6** = 90:10). In contrast, **14e** affords **7** and **8** in nearly equal amounts. The reaction of *Z* sulfoxides is more complicated. If the major intermediate **13z**, matched system, were quenched with deuterium oxide, **8** would be formed preferentially over **7**. Instead, **13z** rotates readily to the mismatched **14e** because of steric repulsion between the phenyl group on the β-carbon and the sulfoxide moiety, giving rise to nonselective formation of **7** and **8**. Similarly the minor intermediate **14z** affords a mixture of **5** and **6** via **13e**, but the contribution of **14z** decreases the selectivity (70:30).

Lastly, the reaction of dialkylcuprates with phenyl vinyl sulfoxide (**1a**) was undertaken to contrast with that of silylcuprate **2**. Unfortunately, Michael adducts **15** were

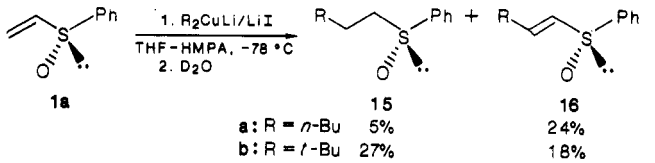
Scheme I



Scheme II



obtained in low yields along with (*E*)-alkenyl sulfoxides **16**, and no deuterium was incorporated in either product.[15]



a: R = *n*-Bu 5% 24%
b: R = *t*-Bu 27% 18%

Stereochemical Assignment. The absolute or relative configuration of the products **3** and **4** was determined as follows (Scheme I). Optically active **4e**, an adduct of **2** and (*E*)- or (*Z*)-1-heptenyl *p*-tolyl (*R*)-sulfoxide (**1e**), was oxidized with *m*-chloroperbenzoic acid to (+) sulfone **17a**. Desulfurization of **17a** with sodium amalgam gave (−)-2-(dimethylphensylsilyl)heptane (**18**),[16] which was converted with retention by Fleming's method[17] to the known (+)-(*S*)-2-heptanol (**19**) (lit.[18] $[\alpha]^{25}_D$ +12.10°). Thus the configuration of **4e** must be R_cR_s. In contrast, oxidation of the other isomer **3e** afforded (−) sulfone **17b** ($[\alpha]^{25}_D$ −13.1°), indicating S_cR_s configuration for **3e**.[19] Furthermore, the structure of the two isomers **3** and **4** was easily elucidated by their NMR spectra and R_f values on silica gel (see Experimental Section).

Configurations of the deuteriated compounds **5**–**8** were determined on the basis of pyrolysis (Scheme II). When the mixture of **5d** and **6d** (90:10) was heated at 100 °C for 15 min, (*E*)- and (*Z*)-deuteriostyrenes **20** and **21** were quantitatively obtained (85:15), along with diphenyl disulfide. Similarly, the mixture of **7d** and **8d** (40:60) afforded **20** and **21** in a ratio of 41:59.

Pyrolysis of **5f**–**8f** gave similar results. Since the elimination of arylsulfenic acid was reported to proceed in a

(14) (a) Hayashi, T.; Okamoto, Y.; Kabeta, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* **1984**, *49*, 4224. (b) Fleming, I.; Hill, J. H. M.; Parker, D.; Waterson, D. *J. Chem. Soc., Chem. Commun.* **1985**, 318.

(15) A tricky behavior of α,β-unsaturated sulfoxides in the reaction with dialkylcuprates was also reported. Hua, D. H.; Venkataraman, S.; Ostrander, R. A.; Sinai, G. Z.; McCann, P. J.; Coulter, M. J.; Xu, M. R. *J. Org. Chem.* **1988**, *53*, 507.

(16) $[\alpha]^{20}_D$ −4.49° (*c* 5.0, benzene) for 45% ee (−)-*S* compound: Hayashi, T.; Konishi, M.; Okamoto, Y.; Kabeta, K.; Kumada, M. *J. Org. Chem.* **1986**, *51*, 3772.

(17) Fleming, I.; Henning, R.; Plaut, H. *J. Chem. Soc., Chem. Commun.* **1984**, 29.

(18) Prout, F. S.; Spinkner, J. E. *J. Org. Chem.* **1962**, *27*, 1488.

(19) A similar structural determination of **3f** and **4f** failed because the desulfurization competed with elimination of the silyl group.

syn manner,[20] the stereochemistry of the four isomers 5–8 was unambiguously established as shown above. In addition, the reaction rate of 7 and 8 was slower than that of 5 and 6.[21] This difference is due to steric hindrance between the silyl and aryl groups in the syn transition state for 7 and 8, providing additional structural evidence for 5–8.

The stereochemistry of the deuteriated sulfones 10 and 11 was confirmed by comparison with authentic samples prepared from 5 + 6 and 7 + 8 mixtures.

Experimental Section

Melting points were measured with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded with a Hitachi 215 spectrophotometer. ^1H and ^{13}C NMR spectra were obtained from a JEOL PMX-60 and a JEOL FX-90 spectrometer, and chemical shifts are reported in parts per million on the δ scale from internal tetramethylsilane. Mass spectra were taken at 20 eV with a Shimadzu GCMS-QP-1000 mass spectrometer. Optical rotations were measured on a JASCO DIP-181 polarimeter. Microanalyses were determined on a Yanagimoto CHN-Corder. Medium-pressure liquid chromatography (MPLC) was performed by using Merck Kieselgel 60 (230–400 mesh ASTM).

Materials. All α,β-unsaturated sulfoxides 1 were prepared by the reported method[22] and separated into *E* and *Z* isomers by MPLC. Optical purity of the chiral sulfoxides **1e** and **1f** was determined by optical rotations: (*E*)-**1e**, $[\alpha]^{31}_D$ + 137° (*c* 0.630, acetone), 92% ee [lit.[23] +148.2° (*c* 0.517, acetone)]; (*Z*)-**1e**, $[\alpha]^{25}_D$ −295° (*c* 0.604, acetone), 97% ee [lit.[23] −304.7° (*c* 0.597, acetone)]; (*E*)-**1f**, $[\alpha]^{29}_D$ +152° (*c* 1.175, $CHCl_3$), 92% ee [lit.[23] +166° (*c* 1.14, $CHCl_3$)]; (*Z*)-**1f**, $[\alpha]^{29}_D$ −714° (*c* 1.035, $CHCl_3$), 97% ee [lit.[23] −736° (*c* 1.04, $CHCl_3$)]. Lithium bis(dimethylphenylsilyl)cuprate (2) and the related copper reagents were generated in situ according to the literature method.[10]

General Procedure for the Reaction of α,β-Unsaturated Sulfoxides 1 with Lithium Bis(dimethylphenylsilyl)cuprate (2). (Dimethylphenylsilyl)lithium (0.8 M in THF, 30 mL) was added under nitrogen to a suspension of copper(I) iodide (2.28 g, 12 mmol) in THF (10 mL) at 0 °C and stirred for 20 min.[10] After the solution was cooled to −78 °C, hexamethylphosphoramide (2.15 g, 12 mmol) was added and stirred for 15 min. Then the sulfoxide 1 (10 mmol) in THF (20 mL) was added to the solution and quenched at −78 °C immediately (for **1a–c**), after 5 min (for **1e**), or after 15 min (for **1d,f**) with aqueous ammonium chloride solution or deuterium oxide (4 mL). The solution was allowed to warm to room temperature and poured into saturated NH_4Cl solution. The reaction mixture was extracted with ether, washed with NH_4Cl solution and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel (hexane–ethyl acetate, 3:1) to give pure adducts 3 (5 + 6) and 4 (7 + 8, eluted first). Since the compounds 3 and 4 decomposed gradually on being set aside at room temperature, it is advisable to keep them below this temperature.

2-(Dimethylphenylsilyl)ethyl phenyl sulfoxide (3a): colorless oil; IR (neat) 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 6 H, $SiMe_2$), 0.78–1.43 (m, 2 H, H_β), 2.43–3.04 (m, 2 H, H_α), 7.09–7.49 (m, 10 H, Ar); MS, *m/e* 162 ($PhMe_2SiCH{=}CH_2^+$, 50), 135 ($PhMe_2Si^+$, 100). Anal. Calcd for $C_{16}H_{20}OSSi$: C, 66.60; H, 7.00. Found: C, 66.65; H, 6.90.

(S_c*R_s*)-2-(Dimethylphenylsilyl)propyl phenyl sulfoxide (3b): colorless oil; IR (neat) 1035 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.21 (s, 3 H, SiMe), 0.22 (s, 3 H, SiMe), 0.87–1.39 (m, 4 H, Me and H_β), 2.78–2.84 (m, 2 H, H_α), 7.29–7.60 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ −5.8, −5.0, 14.4 (CH_3), 15.6 (C_β), 61.9 (C_α), 124.3, 127.7, 129.0, 129.1, 131.0, 133.6, 135.9, 144.1; MS, *m/e* 176 ($PhMe_2SiC(Me){=}CH_2^+$, 24), 161 (176 − Me, 100), 135 ($PhMe_2Si^+$, 28). Anal. Calcd for $C_{17}H_{22}OSSi$: C, 67.49; H, 7.34. Found: C, 67.30; H, 7.31.

(R_c*R_s*)-2-(Dimethylphenylsilyl)propyl phenyl sulfoxide (4b): colorless oil; IR (neat) 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.28 (s, 6 H, $SiMe_2$), 1.23 (d, *J* = 7.2 Hz, 3 H, Me), 1.60–2.02 (m, 1 H, H_β), 2.21–2.94 (m, 2 H, H_α), 7.30–7.73 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ −5.2, 13.4 (CH_3), 14.3 (C_β), 62.7 (C_α), 123.6, 127.7, 129.0, 129.1, 130.5, 133.7, 136.1, 144.8; MS, *m/e* 176 ($PhMe_2SiC(Me){=}CH_2^+$, 25), 161 (176 − Me, 100), 135 ($PhMe_2Si^+$, 30). Anal. Calcd for $C_{17}H_{22}OSSi$: C, 67.49; H, 7.34. Found: C, 67.40; H, 7.28.

(S_c*R_s*)-2-(Dimethylphenylsilyl)heptyl phenyl sulfoxide (3c): colorless oil; IR (neat) 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 3 H, SiMe), 0.26 (s, 3 H, SiMe), 0.79–1.60 (m, 12 H), 2.77 (dd, *J* = 4.6 and 12.9 Hz, 1 H, *pro-R* H_α), 2.97 (dd, *J* = 8.9 and 12.9 Hz, 1 H, *pro-S* H_α), 7.20–7.60 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ −4.8, −4.0, 13.9, 21.1 (C_β), 22.3, 29.0, 30.3, 31.9, 60.7 (C_α), 124.6, 127.8, 129.0, 129.1, 131.0, 133.6, 136.7, 144.1; MS, *m/e* 232 ($PhMe_2SiC(C_5H_{11}){=}CH_2^+$, 21), 135 ($PhMe_2Si^+$, 100). Anal. Calcd for $C_{21}H_{30}OSSi$: C, 70.32; H, 8.45. Found: C, 70.30; H, 8.42.

(R_c*R_s*)-2-(Dimethylphenylsilyl)heptyl phenyl sulfoxide (4c): coloreless oil; IR (neat) 1040 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 3 H, SiMe), 0.31 (s, 3 H, SiMe), 0.78–1.78 (m, 12 H), 2.54 (dd, *J* = 10.8 and 13.1 Hz, 1 H, *pro-R* H_α), 2.80 (dd, *J* = 3.1 and 13.1 Hz, 1 H, *pro*-S H_α), 7.08–7.68 (m, 10 H, Ar); ^{13}C NMR ($CDCl_3$) δ −3.9, 13.9, 20.0 (C_β), 22.3, 28.7, 29.6, 32.0, 61.7 (C_α), 123.8, 127.8, 129.1, 130.6, 133.8, 137.0, 145.3; MS, *m/e* 232 ($PhMe_2SiC(C_5H_{11}){=}CH_2^+$, 51), 135 ($PhMe_2Si^+$, 100). Anal. Calcd for $C_{21}H_{30}OSSi$: C, 70.32; H, 8.45. Found: C, 70.11; H, 8.42.

(S_c*R_s*)-2-(Dimethylphenylsilyl)-2-phenylethyl phenyl sulfoxide (3d): colorless oil; IR (neat) 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H, SiMe), 0.19 (s, 3 H, SiMe), 2.17 (dd, *J* = 3.3 and 12.9 Hz, 1 H, H_β), 2.99 (dd, *J* = 3.3 and 12.9 Hz, 1 H, *pro-R* H_α), 3.62 (t, *J* = 12.9 Hz, 1 H, *pro-S* H_α), 6.82–7.72 (m, 15 H, Ar); ^{13}C NMR ($CDCl_3$) δ −5.8, −4.2, 30.7 (C_β), 58.5 (C_α), 124.8, 125.4, 127.4, 127.7, 128.3, 128.9, 129.4, 131.2, 133.8, 135.2, 139.4, 143.1; MS, *m/e* 238 ($PhMe_2SiC(Ph){=}CH_2^+$, 66), 135 ($PhMe_2Si^+$, 100). Anal. Calcd for $C_{22}H_{24}OSSi$: C, 72.47; H, 6.65. Found: C, 72.30; H, 6.56.

(R_c*R_s*)-2-(Dimethylphenylsilyl)-2-phenylethyl phenyl sulfoxide (4d): white crystals; 114.5–115.5 °C dec; IR (neat) 1045 (S=O)cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.25 (s, 3 H, SiMe), 0.26 (s, 3 H, SiMe), 2.90–3.29 (m, 3 H, H_α and H_β), 6.86–7.73 (m, 15 H, Ar); ^{13}C NMR ($CDCl_3$) δ −5.1, −4.1, 30.7 (C_β), 61.0 (C_α), 123.6, 125.6, 127.7, 128.1, 128.3, 129.0, 129.4, 130.5, 134.0, 135.5, 139.3, 145.1; MS, *m/e* 238 ($PhMe_2SiC(Ph){=}CH_2^+$, 50), 135 ($PhMe_2Si^+$, 100). Anal. Calcd for $C_{22}H_{24}OSSi$: C, 72.47; H, 6.65. Found: C, 72.22;, H, 6.51.

(+)-(S_cR_s)-2-(Dimethylphenylsilyl)heptyl *p*-tolyl sulfoxide (3e): colorless oil; IR (neat) 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.22 (s, 6 H, $SiMe_2$), 0.70–1.66 (m, 12 H), 2.41 (s, 3 H), 2.76 (dd, *J* = 4.1 and 12.7 Hz, 1 H, *pro-R* H_α), 2.96 (dd, *J* = 9.0 and 12.7 Hz, 1 H, *pro-S* H_α), 7.09–7.31 (m, 9 H, Ar); ^{13}C NMR ($CDCl_3$) δ −4.7, −3.9, 14.0, 21.2 (C_β), 21.4, 22.4 29.1, 30.4, 32.0, 60.8 (C_α), 124.9, 127.8, 129.1, 129.8, 133.7, 136.9, 141.6; MS, *m/e* 232 ($PhMe_2SiC(C_5H_{11}){=}CH_2^+$, 21), 135 ($PhMe_2Si^+$, 100); $[\alpha]^{23}_D$ +28.6° (*c* 0.620, acetone). Anal. Calcd for $C_{22}H_{32}OSSi$: C, 70.90; H, 8.67. Found: C, 70.85; H, 8.51.

(+)-(R_cR_s)-2-(Dimethylphenylsilyl)heptyl *p*-tolyl sulfoxide (4e): colorless oil; IR (neat) 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.30 (s, 6 H, $SiMe_2$), 0.71–1.84 (m, 12 H), 2.40 (s, 3 H), 2.50 (dd, *J* = 10.7 and 13.0 Hz, 1 H, *pro-R* H_α), 2.80 (dd, *J* = 2.9 and 13.0 Hz, 1 H, *pro-S* H_α), 7.11–7.56 (m, 9 H, Ar); ^{13}C NMR ($CDCl_3$) δ −3.9, 14.0, 20.1 (C_β), 21.3, 22.4, 28.8, 29.7, 32.1, 61.8 (C_α), 123.9, 127.9, 129.2, 129.9, 133.9, 137.2, 141.1, 142.1; MS, *m/e* 232 ($PhMe_2SiC(C_5H_{11}){=}CH_2^+$, 20), 135 ($PhMe_2Si^+$, 100); $[\alpha]^{25}_D$ +214° (*c* 0.610, acetone). Anal. Calcd for $C_{22}H_{32}OSSi$: C, 70.90; H, 8.67. Found: C, 70.62; H, 8.53.

(−)-(S_cR_s)-2-(Dimethylphenylsilyl)-2-phenylethyl *p*-tolyl sulfoxide (3f): white crystals; mp 104–105 °C dec; IR (Nujol) 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.10 (s, 3 H, SiMe), 0.19 (s, 3 H, SiMe), 2.12 (dd, *J* = 3.3 and 12.7 Hz, 1 H, H_β), 2.42 (s, 3 H), 2.97 (dd, *J* = 3.3 and 12.7 Hz, 1 H, *pro-R* H_α), 3.61 (t, *J* = 12.7 Hz, 1 H, *pro-S* H_α), 6.79–7.76 (m, 14 H, Ar); ^{13}C NMR ($CDCl_3$) δ −5.7, −4.1, 21.5, 31.0 (C_β), 58.6 (C_α), 125.1, 125.5, 127.6, 127.8, 128.4, 129.5, 129.7, 133.9, 135.4, 139.6, 139.8, 141.8; MS, *m/e* 238

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(21) For example, the ratio of the starting sulfoxides to the styrenes was 7:93 for the **5d** + **6d** mixture and 28:74 for **7d** + **8d** after 19 h at 60 °C in $CDCl_3$.
(22) Solladie, G. *Synthesis* **1981**, 185 and references cited therein.
(23) Kosugi, H.; Kitaoka, M.; Tagami, K.; Takahashi, A.; Uda, H. *J. Org. Chem.* **1987**, *52*, 1078.

($PhMe_2SiC(Ph)=CH_2^+$, 92), 223 (238 - Me, 100), 135 ($PhMe_2Si^+$, 55), $[\alpha]^{29}_D$ -99.1° (*c* 1.335, $CHCl_3$). Anal. Calcd for $C_{23}H_{26}OSSi$: C, 72.95; H, 6.93. Found: C, 72.95; H, 6.90.

(+)-(R_cR_s)-2-(Dimethylphenylsilyl)-2-phenylethyl *p*-tolyl sulfoxide (4f): white crystals; mp 120–121 °C dec; IR (Nujol) 1035 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.24 (s, 6 H, SiMe), 2.34 (s, 3 H), 2.97–3.16 (m, 3 H, H_α and H_β), 7.03–7.43 (m, 14 H, Ar); ^{13}C NMR ($CDCl_3$) δ -5.1, -4.3, 21.2, 30.7 (C_β), 61.0 (C_α), 123.7, 125.5, 127.2, 128.2, 128.3, 129.4, 129.8, 134.0, 135.6, 139.4, 141.0, 141.9; MS, *m/e* 238 ($PhMe_2SiC(Ph)=CH_2^+$, 65), 223 (238 - Me), 87), 135 ($PhMe_2Si^+$, 100), $[\alpha]^{29}_D$ +123° (*c* 1.300, $CHCl_3$). Anal. calcd for $C_{23}H_{26}OSSi$: C, 72.95; H, 6.93. Found: C, 72.78; H, 6.77.

Aryl 1-Deuterio-2-(dimethylphenylsilyl)-2-phenylethyl Sulfoxides (5d,f–8d,f). Two mixtures of the deuteriated sulfoxides, **5** + **6** and **7** + **8**, showed spectral data similar to those of **3** and **4**, respectively. But two doublets for α-protons in the ^1H NMR spectra and a triplet for α-carbon in the ^{13}C NMR spectra were observed as expected. The product ratio of the mixtures was determined by ^1H NMR directly and/or after oxidation to the corresponding sulfones.

Reaction of Aryl Styryl Sulfones 9 with the Cuprate 2. The sulfone **9** (1.0 mmol) in THF (2 mL) was added under nitrogen to a solution of the cuprate **2** (1.2 mmol) in THF (6 mL) containing HMPA (1.2 mmol) at -78 °C and stirred for 15 min. Then the reaction was quenched with deuterium oxide (0.5 mL). After the usual workup, purification by MPLC (hexane–ethyl acetate, 2:1) gave a crystalline mixture of the sulfones **10** and **11** in 85–90% yields, whose ratio was determined by ^1H NMR. The sulfones **10** and **11** and the related sulfones containing no deuterium were also prepared quantitatively from the corresponding sulfoxides **3–8** by the oxidation with *m*-chloroperbenzoic acid.

2-(Dimethylphenylsilyl)-2-phenylethyl phenyl sulfone: white crystals; mp 120–133 °C dec from CCl_4; IR (Nujol) 1300, 1135 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.18 (s, 3 H, SiMe), 0.21 (s, 3 H, SiMe), 2.87 (dd, *J* = 2.4 and 12.0 Hz, 1 H, H_β), 3.33 (dd, *J* = 2.4 and 14.7 Hz, 1 H, H_α anti to Ph), 3.68 (dd, *J* = 12.0 and 14.7 Hz, 1 H, H_α syn to Ph), 6.52–7.66 (m, 15 H, Ar); ^{13}C ($CDCl_3$) δ -5.8, -4.2, 31.5 (C_β), 57.0 (C_α), 125.1, 127.4, 127.8, 128.4, 129.6, 132.8, 133.9, 134.9, 138.1, 139.7; MS, *m/e* 276 ($PhMe_2SiO_2SPh^+$, 25), 261 (276 - Me, 100), 135 ($PhMe_2Si^+$, 86). Anal. Calcd for $C_{22}H_{24}O_2SSi$: C, 69.42; H, 6.37. Found: C, 69.16; H, 6.34.

2-(Dimethylphenylsilyl)-2-phenylethyl *p*-Tolyl Sulfone. (+)-*R* isomer: prepared from **4f**; white crystals; mp 126.5–127.5 °C dec from CCl_4; IR (Nujol) 1300, 1140 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.16 (s, 3 H, SiMe), 0.20 (s, 3 H, SiMe), 2.27 (s, 3 H, Me), 2.84 (dd, *J* = 2.3 and 12.0 Hz, 1 H, H_β), 3.31 (dd, *J* = 2.3 and 14.7 Hz, 1 H, H_α anti to Ph), 3.66 (dd, *J* = 12.0 and 14.7 Hz, 1 H, H_α syn to Ph), 6.60–7.62 (m, 14 H, Ar); ^{13}C NMR ($CDCl_3$) δ -5.8, -4.2, 21.3, 31.5 (C_β), 57.1 (C_α), 124.8, 127.5, 127.8, 127.9, 129.1, 129.5, 133.9, 135.0, 136.6, 138.3, 143.6; MS, *m/e* 290 ($PhMe_2SiO_2STol\text{-}p^+$, 31), 213 (290 - Ph, 100), 135 ($PhMe_2Si^+$, 63); $[\alpha]^{28}_D$ +16.3° (*c* 1.042, acetone). Anal. Calcd for $C_{23}H_{26}O_2SSi$: C, 70.00; H, 6.65. Found: C, 69.99; H, 6.60. **(-)-*S* isomer**: prepared from **3f**; white crystals; mp 144–145 °C dec from CCl_4; $[\alpha]^{28}_D$ -14.8° (*c* 1.024, acetone).

Reaction of Phenyl Vinyl Sulfoxide (1a) with Lithium Dialkylcuprate. The sulfoxide **1a** (304 mg, 2.0 mmol) in THF (5 mL) was added under nitrogen at -78 °C to a solution of lithium di-*n*-butylcuprate, prepared from *n*-butyllithium (1.6 M in hexane, 3 mL) and copper(I) iodide (457 mg, 2.4 mmol), in THF (15 mL), and stirred for 3 h at 0 °C. The reaction was quenched with deuterium oxide (1 mL). After the usual workup, purification of the mixture by MPLC using hexane–ethyl acetate (3:1) gave *n*-hexyl phenyl sulfoxide (**15a**) (21 mg, 5%) and (*E*)-1-hexenyl phenyl sulfoxide (**16a**) (100 mg, 24%). **15a**: ^1H NMR ($CDCl_3$) 0.70–1.92 (m, 11 H), 2.69 (br t, *J* = 6.0 Hz, 2 H), 7.34–7.75 (m, 5 H); MS, *m/e* 210 (M^+). **16a**: ^1H NMR ($CDCl_3$) δ 0.77–1.62 (m, 7 H), 2.03–2.47 (m, 2 H), 6.21 (d, *J* = 15.0 Hz, 1 H), 6.66 (dt, *J* = 6.0 and 15.0 Hz, 1 H), 7.37–7.73 (m, 5 H); MS, *m/e* 208 (M^+). Anal. Calcd for $C_{12}H_{16}OS$: C, 69.18; H, 7.76. Found: C, 68.88; H, 7.46. Similar reaction of the sulfoxide **1a** with di-*tert*-butylcuprate gave 3,3-dimethylbutyl phenyl sulfoxide (**15b**), 27%, and (*E*)-3,3-dimethyl-1-butenyl phenyl sulfoxide (**16b**), 18%. **15b**: ^1H NMR ($CDCl_3$) δ 0.84 (s, 9 H), 1.32–1.68 (m, 2 H), 2.58–2.95 (m, 2 H) 7.37–7.67 (m, 5 H); MS, *m/e* 210 (M^+). **16b**: ^1H NMR ($CDCl_3$) δ 1.07 (s, 9 H), 6.12 (d, *J* = 15.0 Hz, 1 H), 6.65 (d, *J* = 15.0 Hz, 1 H), 7.37–7.73 (m, 5 H); MS, *m/e* 208 (M^+).

Stereochemical Assignment of 3e and 4e. The sulfoxide **4e** (1.142 g, 3.1 mmol) was treated with MCPBA (0.583 g, 3.4 mmol) in dry dichloromethane (40 mL) at room temperature for 1 h. The mixture was poured into aqueous sodium thiosulfate solution, extracted with dichloromethane, washed with sodium hydrogen carbonate, dried ($MgSO_4$), and concentrated in vacuo. The residue was chromatographed on silica gel (hexane–ethyl acetate, 3:1) to give (+)-(*R*)-2-(dimethylphenylsilyl)heptyl *p*-tolyl sulfone (**17a**): 1.189 g (100%); colorless oil; IR (neat) 1310, 1140 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.27 (s, 6 H, $SiMe_2$), 0.69–1.74 (m, 12 H), 2.43 (s, 3 H) 3.02 (m, 2 H), 7.24–7.70 (m, 9 H); ^{13}C NMR ($CDCl_3$) δ -4.5, -3.7, 14.0, 20.4, 21.5, 22.3, 28.3, 29.3, 32.0, 57.3, 127.9, 129.2, 129.7, 133.7, 136.7, 137.1, 144.1; MS, *m/e* 373 (M^+ - Me, 3), 290 ($PhMe_2SiO_2STol\text{-}p^+$, 8), 135 ($PhMe_2Si^+$, 100); $[\alpha]^{31}_D$ +13.7° (*c* 0.665, acetone). Anal. Calcd for $C_{22}H_{32}O_2SSi$: C, 67.98; H, 8.32. Found: C, 67.80; H, 8.22. (-)-*S*-sulfone **17** [$[\alpha]^{25}_D$ -13.1° (*c* 0.650, acetone)] was obtained similarly from **3e**.

The (+)-*R* sulfone **17a** (1.025 g, 2.64 mmol) was refluxed with 5% sodium amalgam (19.0 g) in ethanol (40 mL) for 12 h. After cooling to room temperature, aqueous sodium hydroxide solution (3%, 5 mL) was added to the solution and stirred for 1 h. The mixture was decanted, and the residue was rinsed with ethanol. The combined solution was concentrated in vacuo, extracted with ether, washed with sodium hydrogen carbonate solution and brine, and dried ($MgSO_4$). Evaporation of the solvent gave a yellow residue, which was purified by MPLC (hexane) to afford (-)-(*S*)-2-(dimethylphenylsilyl)heptane (**18**):[16] 565 mg (91%); colorless oil; ^1H NMR ($CDCl_3$) δ 0.24 (s, 6 H, $SiMe_2$), 1.74–2.60 (m, 15 H), 7.17–7.60 (m, 5 H, Ar); ^{13}C NMR ($CDCl_3$) δ -4.8, 0, 14.1, 19.1, 22.6, 28.3, 31.7, 31.9, 127.6, 128.7, 133.9, 139.0; $[\alpha]^{25}_D$ -14.2° (*c* 2.555, benzene).

Boron trifluoride–acetic acid complex (40%, 0.4 mL) was added under nitrogen to a solution of the (-)-(*S*)-heptane **18** (307 mg, 1.31 mmol) in dichloromethane (8 mL) at 0 °C and stirred for 2 h at room temperature. The mixture was poured into cooled sodium hydrogen carbonate solution, extracted with ether, washed with brine, dried ($MgSO_4$), and concentrated in vacuo to leave crude 2-(dimethylfluorosilyl)heptane (197 mg, 85%). Then the crude (fluorosilyl)heptane (186 mg, 1.06 mmol) was treated under nitrogen with MCPBA (640 mg, 3.71 mmol) and KF (215 mg, 3.71 mmol) in dimethylformamide (20 mL) for 40 h at room temperature. Aqueous workup and purification by MPLC gave (+)-(*S*)-2-heptanol (**19**), which was identified with a commercially available authentic sample: 75 mg (52% from **18**); $[\alpha]^{25}_D$ +12.1° (*c* 0.655, ethanol) (lit.[18] $[\alpha]^{25}_D$ +12.10°).

Pyrolysis of the Deuteriated Sulfoxides 5–8. A crystalline mixture of **5d** and **6d** (90:10), or **7d** and **8d** (40:60) (~30 mg) was heated at 100 °C for 15 min in an NMR tube, and the resulting yellow liquid was diluted with $CDCl_3$ containing dimethyl sulfoxide as internal standard. Their ^1H NMR spectra indicated the formation of the deuteriated styrenes **20** and **21** (>90% yield, 85:15 from **5d** + **6d**, 41:59 from **7d** + **8d**), along with diphenyl disulfide (50%). The pyrolysis was also performed in $CDCl_3$ solution in the presence or absence of triethylamine at 60 °C, or in a preparative GC column (200 °C). Predominant formation of **20** from **5d** + **6d** and **21** from **7d** + **8d** was observed in every case, but the selectivity was decreased as temperature and time increased. A similar result was obtained in the pyrolysis of **5f–8f**. The structure and ratio of the styrenes **20** and **21** were confirmed by comparing their spectral data to those of α-(dimethylphenylsilyl)styrene, an authentic sample, prepared from α-lithiostyrene and dimethylphenylsilyl chloride (59% yield): colorless oil; bp 160 °C (3 Torr, Kugelrohr); IR (neat) 1580 (C=C) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.41 (s, 6 H, $SiMe_2$), 5.67 (d, *J* = 2.9 Hz, 1 H, (*Z*)-SiC=C*H*, 8.5% NOE effect by $SiMe_2$), 5.98 (d, *J* = 2.9 Hz, 1 H, (*E*)-SiC=C*H*), 6.83–7.57 (m, 10 H, Ar); MS, *m/e* 238 (M^+, 85), 223 (M^+ - Me, 100). Anal. Calcd for $C_{16}H_{18}Si$: C, 80.61; H, 7.61. Found: C, 80.60; H, 7.58.