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Further Evidence to Understand the Stereochemistry of the Reactions of α-Sulfinyl Carbanions

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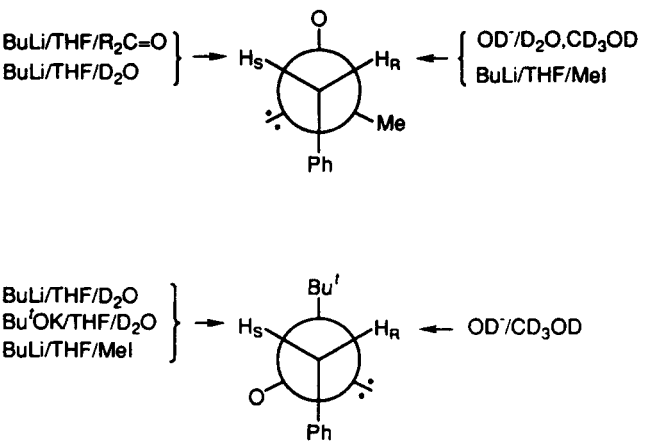
ABSTRACT

The stereochemistry of the α-sulfinyl carbanion has been studied. It has been elucidated that a 2-pyridylmethyl substituent on the sulfinyl sulfur chelates onto the counter cation in an ion pair to fix the conformation of the anion at a particular orientation. Then, the steric bulk of the other substituent plays a role to control the reacting face. A soft electrophile such as methyl iodide attacks the anion from the more open side. On the other hand, a hard electrophile such as a proton is initially trapped by the polar part of the ion pair and no steric effect operates.

Although the stereochemistry of the reactions of α-sulfinyl carbanions have been studied for a long period by many chemists [1–6], there still remain several questions on the stereochemical course of the reactions. Namely, different stereochemical results have been seen in the reactions of carbanions that have different sulfinyl-substituents. Also, the difference in the stereochemistry of the reaction of a sulfinyl carbanion with different electrophiles has not yet been explained by a unified concept. For example, methylation by methyl iodide and deuteronation by deuterium oxide proceed on methyl- and *t*-butylsulfinyl carbanions ($\mathbf{1_C}^-$ and $\mathbf{2_C}^-$), respectively, as depicted in Scheme 1 [7].

Based on ^{1}H NMR spectroscopy, we proposed



SCHEME 1

that the bulkiest group/atom substituent on the sulfur is the oxygen in $\mathbf{1_C}$, whereas the *t*-butyl group is the largest in $\mathbf{2_C}$ [7]. Assuming that the proton abstractions from $\mathbf{1_C}$ and $\mathbf{2_C}$ by a base take place *via* these stable conformations of the parent compounds, we suggested that the carbanions can induce soft and hard faces and that a soft electrophile attacks the carbanion mainly from the soft face and *vice versa* (Scheme 2) [8]. The stereospecificity of the reaction with the anion derived from phenylmethyl *p*-tolyl sulfoxide ($\mathbf{3_C}^-$) is extremely low [9], because the steric bulk of the *p*-tolyl group on the sulfur atom is of medium magnitude and cannot contribute to freeze the conformation at a particular position.

At the same time, it has been reported that the so-called "carbanions" are not truly carbanions but are explained best as dimeric oxylate anions both in solution [10–12] and in the crystal [13]. In other

Dedicated to Professor Yao-Zeng Huang on the occasion of his eightieth birthday.

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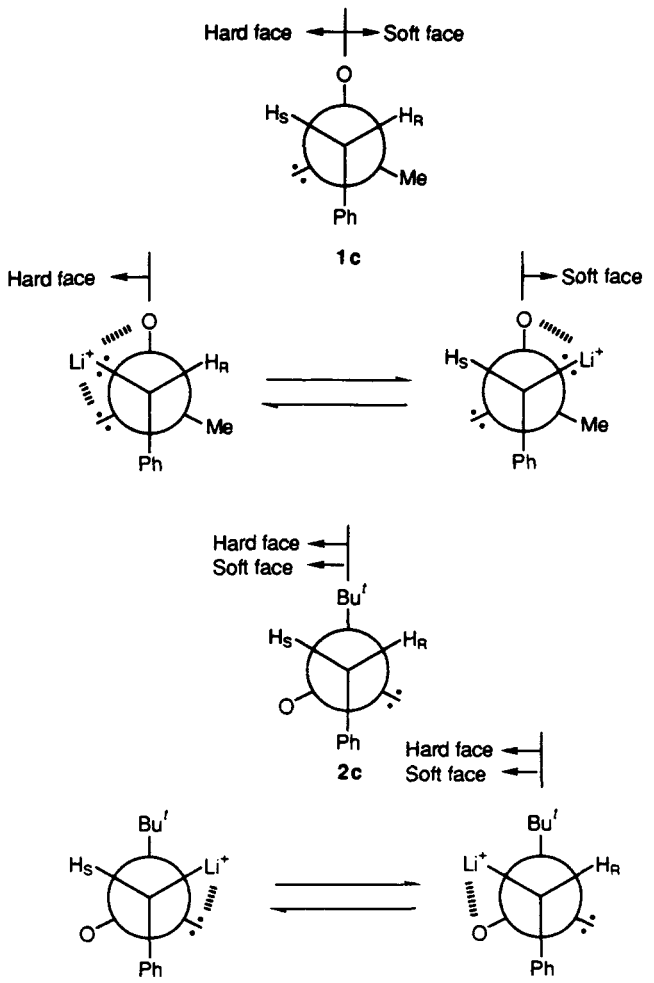
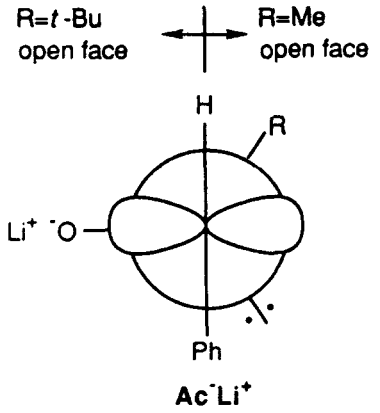


SCHEME 2

words, the formally anionic carbon α to the sulfinyl group has the sp^2 configuration, and the steric bulk of the sulfinyl oxygen in relation to its vicinity is much larger than that expected from the formal carbanion structure, because it is involved in a bridging component of the dimer. The steric bulk of the substituents on the sulfur atom thus changes significantly on going from a sulfoxide to the corresponding sulfinyl anion, and the conformation in the parent sulfoxide can no longer be retained in the derived anion.

Based on the results of X-ray crystallography, Boche proposed that the sulfinyl lone-pair electrons always maintain the position gauche to the large phenyl group, keeping the sulfinyl oxygen at the eclipsed position with respect to the *p*-lobe of the sp^2-carbanion regardless of the bulkiness of the alkyl substituent ($\mathbf{A_C}^-$ Li^+) [14]. It has been confirmed that at least the carbanion similar to $\mathbf{2_C}^-$ assumes this conformation in a crystal [13]. The electrophile always attacks these anions, mainly from the open face; the face which includes the methyl group is the open side in $\mathbf{1_C}^-$, whereas the *t*-butyl group contributes to a closed face of $\mathbf{2_C}^-$ by its bulkiness. The idea also serves to explain the stereochemical course of the reaction.



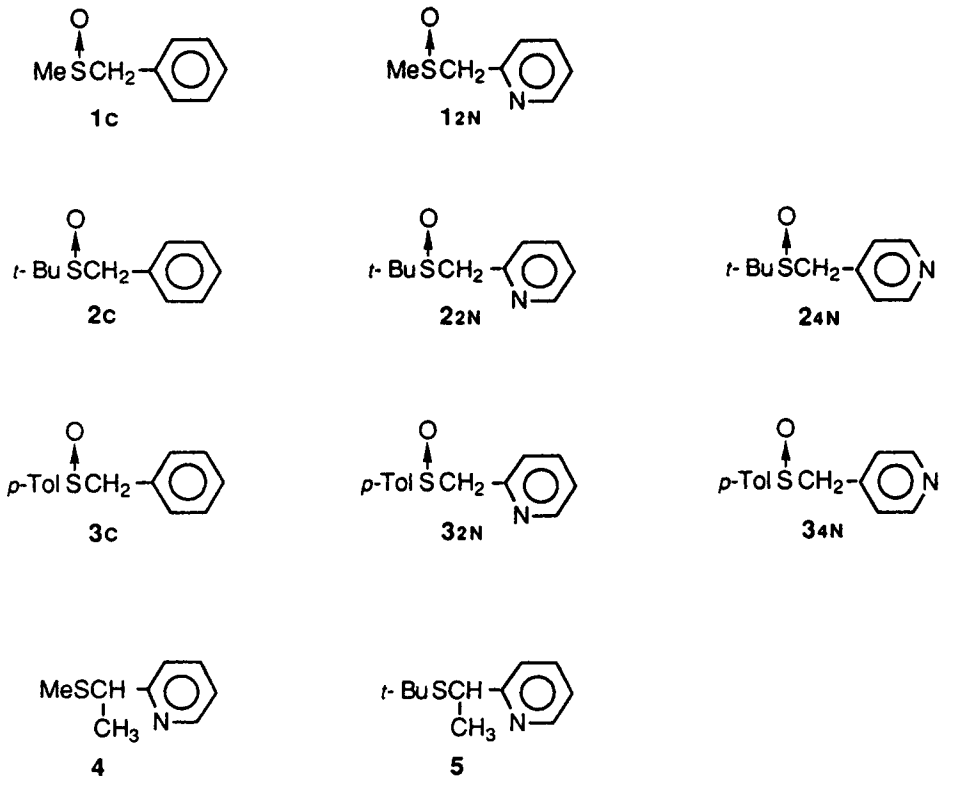
It is interesting to test which of the two proposals explains the observed phenomena better and reflects the property of the anion more appropriately.

When the phenyl group in $\mathbf{1_C}$ and $\mathbf{2_C}$ is substituted by a 2-pyridyl group, the counter cation might be chelated intramolecularly by the pyridyl nitrogen as well as by the sulfinyl oxygen which is the real anionic center. Consequently, the conformations of these "oxylate" anions derived from methyl and *t*-butyl 2-pyridyl methyl sulfoxides ($\mathbf{1_{2N}}^-$ and $\mathbf{2_{2N}}^-$) must be different from those in $\mathbf{1_C}^-$ and $\mathbf{2_C}^-$, respectively. The same will also be true for $\mathbf{3_C}^-$ and the anion from 2-pyridyl methyl *p*-tolyl sulfoxide ($\mathbf{3_{2N}}^-$).

Inspection of the stereochemistry of reactions of these anions with certain electrophiles can help to evaluate the validity of the explorations by us and by Boche and his co-workers. Of course, Boche's explanation of the steric effect does not work with water (protonation/deuteronation). There remains no doubt that such a polar reagent as water is initially attracted by a polar part of the dimer. Thus, the face which includes the counter cation predominates over the other in attracting the polar electrophile.

RESULTS AND DISCUSSION

In addition to the sulfoxides, $\mathbf{1_C}$, $\mathbf{1_{2N}}$, $\mathbf{2_C}$, and $\mathbf{2_{2N}}$, *t*-butyl 4-pyridylmethyl sulfoxide ($\mathbf{2_{4N}}$) was also studied to confirm the validity of ignoring the purely electronic effect of the pyridyl group. The corresponding comparison of the stereochemistry in the reaction of $\mathbf{3_C}$ and $\mathbf{3_{2N}}$ with that of 4-pyridylmethyl *p*-tolyl sulfoxide ($\mathbf{3_{4N}}$) was reported by Furukawa *et al.* [5] The results reported in the literature [5] will also be included in the discussion in this report. Since all sulfoxides so far studied have the same configuration with respect to the stereochemistry at the sulfur atom, we neglect the in-



SCHEME 3

dication of the configuration at the sulfinyl sulfur for simplicity of the discussion, and, hereafter, the anion will be explained as if it were an enantiotopic species. Methylation of the anion that was derived from the sulfoxide by deprotonation with butyllithium in tetrahydrofuran (THF) was studied mainly by using methyl iodide as an electrophile, because the stereochemistry of the reactions with nonpolar electrophiles has been the subject of controversy [15]. The results are summarized in Table 1. In order to determine the absolute configuration of the products, the sulfoxides that were formed were reduced to their corresponding sulfides and the configurations of the sulfides thus obtained were determined by comparing their optical rotations with those of corresponding authentic samples.

There are remarkable tendencies observable in Table 1; (1) the stereospecificity is inverted in a series of *t*-butyl sulfoxides by changing the substituent from the phenylmethyl group to the 2-pyridylmethyl group (from $\mathbf{2_C}$ to $\mathbf{2_{2N}}$), whereas it remains unchanged in a series of methyl sulfoxides (from $\mathbf{1_C}$ to $\mathbf{1_{2N}}$); (2) in a series of *p*-tolyl sulfoxides, the substitution of the phenylmethyl group by the 2-pyridylmethyl group (from $\mathbf{3_C}$ to $\mathbf{3_{2N}}$), improves the stereospecificity appreciably; (3) the substitution of the phenylmethyl group by the 4-pyridylmethyl group (from $\mathbf{2_C}$ to $\mathbf{2_{4N}}$ or from $\mathbf{3_C}$ to $\mathbf{3_{4N}}$) does not affect the stereochemical results, thus confirming the concept of no contribution of the electronic effect to the stereochemistry; and (4) a change of the reaction temperature does not result in a practical change in stereospecificity.

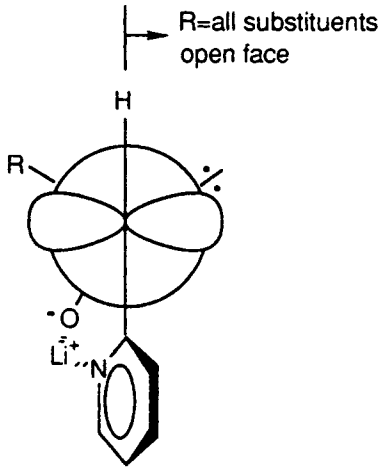
TABLE 1 Methylation of Anions Derived from Various Sulfoxides by Methyl Iodide in THF

Run	Sulfoxide	Temperature (°C)	Methylated Position		Chemical Yield (%)
			H_S	H_R	
1	$\mathbf{1_C}$[a]	−78	4	96	76
2	$\mathbf{1_{2N}}$	−78	13	87	57
3	$\mathbf{2_C}$[a]	−78	99	1	95
4	$\mathbf{2_C}$	25	97	3	97
5	$\mathbf{2_{2N}}$	−78	25	75	77
6	$\mathbf{2_{2N}}$	25	26	74	73
7	$\mathbf{2_{4N}}$	−20	89	11	56
8	$\mathbf{3_C}$[b]	−78	30	70	94
9	$\mathbf{3_{2N}}$[c]	−78	9	91	89
10	$\mathbf{3_{4N}}$[c]	−20	48	52	—

[a]Data taken from Ref. 15.
[b]Data taken from Ref. 9.
[c]Data taken from Ref. 5.

It has been reported that the chelation of the counter lithium cation by an amine nitrogen in an

ion pair of an enolate derived from an amino ketone stabilizes the species by 3–5 kcal/mol [16]. When a similar chelation by the 2-pyridyl nitrogen is expected for the counter lithium cation in the ion pairs, $\mathbf{1}_{2N}^{-}Li^{+}$, $\mathbf{2}_{2N}^{-}Li^{+}$, and $\mathbf{3}_{2N}^{-}Li^{+}$, the most stable conformation of the ion pair is the one represented by $\mathbf{B}_{2N}^{-}Li^{+}$. The fact that the 4-pyridyl substituent behaves similarly to the phenyl substituent at the same position strongly supports the idea that the 2-pyridyl substituent plays a crucial role in the stereochemistry of present interest.



$\mathbf{B}_{2N}^{-}Li^{+}$

In the conformation $\mathbf{B}_{2N}^{-}Li^{+}$, the lithium cation locates on the central Py-H line and does not construct the hard face of the anion. If the stereoelectronic effect of the sulfur lone pair operates to create the soft face, as previously proposed by us, the methylation should occur from the left-hand side, resulting in the formation of the (*S*)-product, which is different from the observed result. All anions afford the (*R*)-product regardless of the bulkiness of the alkyl substituent. It is noteworthy that even the *p*-tolylsulfinyl compound exerts a very high stereospecificity when the *p*-tolyl group is substituted by a 2-pyridylmethyl group ($\mathbf{3}_{2N}$ *vs.* $\mathbf{3}_{C}$ and $\mathbf{3}_{4N}$). Thus, it has been clearly confirmed that the stereoelectronic effect of the lone pair on the sulfur atom does not overcome the steric inhibition by the alkyl substituent on the sulfinyl sulfur. In this sense, Boche's proposal that the relative bulkiness of the substituents defines the face of the electrophilic attack seems correct when one accepts the idea that the conformation observed in a crystal is also held in solution. As mentioned previously, it has been proven that the electronic structure of the anion is the same in both the solid and solution states [10–13]. In the series of compounds substituted by a 2-pyridyl group, the electrophile always approaches at the face of the smallest lone pair, or the open face.

TABLE 2 Methylation of the Anions Derived from *t*-Butyl (2-Pyridyl)methyl Sulfoxide ($\mathbf{2}_{2N}$) in Various Solvent Systems

Run	Solvent System	Temperature (°C)	Methylated Position H_S	Methylated Position H_R
1	Toluene[a]	−20	3	97
2	Toluene	25	6	94
3	Toluene-THF[b]	−78	8	92
4	Toluene-THF[c]	−78	11	89
5	Toluene-HMPA[d]	−78	20	80
6	Toluene-12-crown-5[d]	−78	27	73
7	Toluene-DMAP[e,f]	−78	26	74
8	THF	25	26	74
9	THF	−78	25	75

[a]The ion pair does not dissolve in toluene at −78°C.
[b]Two equivalent amounts.
[c]Ten equivalent amounts.
[d]Three equivalent amounts.
[e]Five equivalent amounts.
[f]4-Dimethylaminopyridine.

Stereospecificity of the reaction with $\mathbf{2}_{2N}$ is lower than those of the others. The result stems from the fact that the reacting face of this anion is opposite that of $\mathbf{2}_{C}$; partial contribution of another conformer, $\mathbf{A}_{C}^{-}Li^{+}$ (or the $\mathbf{2}_{C}$-type), in thermodynamic equilibrium may reduce the specificity. The contribution of another conformer (or conformers) is proven by the solvent effect; that is, if plural conformations exist in a solution, the reaction in a less chelating solvent may emphasize the chelating contribution of the 2-pyridyl group, thus making the conformation $\mathbf{B}_{2N}^{-}Li^{+}$ more important.

Table 2 compares the stereospecificity of the reactions with $\mathbf{2}_{2N}^{-}Li^{+}$ in different solvents or solvent mixtures. Apparently, the reaction in a nonpolar solvent, toluene, exerts the best specificity. The facts that the addition of only 2 equiv amounts of THF, which has a high coordinating ability [17], to the toluene system results in a remarkable decrease in the specificity and that the addition of the more coordinating hexamethylphosphoramide (HMPA) or a crown ether further reduces the specificity to the level of pure THF strongly suggest that the coordination of a polar solvent molecule to the counter lithium cation in the ion pair is quite specific and can compete with the internal chelation by heteroatoms in the molecule.

The importance of chelation in maintaining the conformation can also be seen in the effect of the counter cation: when the lithium salt is substituted by a more dissociating potassium salt, the stereochemistry of methylation is reversed in the reaction with $\mathbf{2}_{2N}$, whereas it stays constant in the reactions with $\mathbf{2}_{C}$ and $\mathbf{2}_{4N}$ (Table 3). In the former reaction, the reacting conformation changes de-

TABLE 3 Effect of the Counter Cation on the Stereochemistry of Methylation of *t*-Butyl Sulfoxides, $\mathbf{2_{2N}}$ and $\mathbf{2_C}$, and $\mathbf{2_{4N}}$ at −78°C

Run	Sulfoxide	Base	Solvent	Methylated Position H_S	Methylated Position H_R
1	$\mathbf{2_{2N}}$	BuLi	THF	25	75
2	$\mathbf{2_{2N}}$	BuLi	Toluene[a]	3	97
3	$\mathbf{2_{2N}}$	*t*-BuOK	THF	93	7
4	$\mathbf{2_{2N}}$	KH	Toluene	92	8
5	$\mathbf{2_C}$	BuLi	THF	99	1
6	$\mathbf{2_C}$	BuLi	Toluene[a]	99	1
7	$\mathbf{2_C}$	*t*-BuOK	THF	99	1
8	$\mathbf{2_{4N}}$	BuLi	THF[a]	89	11
9	$\mathbf{2_{4N}}$	*t*-BuOK	THF[a]	95	5

[a]At −20°C. When the salt was unable to dissolve in the solvent at −78°C, higher temperatures were employed.

TABLE 4 Deutrontion of Anions Derived from Various Sulfoxides by an Acid in THF at −78°C

Run	Sulfoxide	Acid	Deutronated Positions H_S	Deutronated Positions H_R
1	$\mathbf{1_{2N}}$	CH_3CO_2D	55	45
2	$\mathbf{1_{2N}}$[a]	CH_3CO_2D	51	49
3	$\mathbf{1_{2N}}$	DCl/D_2O	59	41
4	$\mathbf{1_C}$	CH_3CO_2D	82	18
5	$\mathbf{1_C}$[a]	CH_3CO_2D	85	15
6	$\mathbf{1_C}$	DCl/D_2O	94	16
7	$\mathbf{2_{2N}}$	CH_3CO_2D	70	30
8	$\mathbf{2_{2N}}$[a]	CH_3CO_2D	58	42
9	$\mathbf{2_{2N}}$	DCl/D_2O	74	26
10	$\mathbf{2_C}$	CH_3CO_2D	83	17
11	$\mathbf{2_C}$[a]	CH_3CO_2D	97	3
12	$\mathbf{2_C}$	DCl/D_2O	99	1

[a]At −20°C in toluene.

pending on the presence or absence of the chelation dependent on the counter cation, whereas the intramolecular chelation is always absent in the latter reactions.

To the authors' best knowledge, there has been no example in which the stereochemistry of the alkylation of an α-sulfinyl carbanion is controlled by the alkali metal counter cation.

As described earlier, the series of compounds with the 2-pyridyl substituent has no hard face and the preferential face in the attack by a hard electrophile such as water/hydronium ion is ambiguous. The reaction was also studied, and the results are summarized in Table 4. As expected, the specificity of the hydronation (protonation/deuteronation) in the series of 2-pyridyl compounds is much lower than that in the case of the corresponding phenyl compound. It is now proven that the water molecule is initially attracted to the polar part of the ion pair. The steric bulk of the substituents plays only a secondary role in defining the preferential attacking face for such hard electrophiles.

EXPERIMENTAL

Melting points were not corrected. ^{1}H NMR spectra were recorded at 200 and 400 MHz on Varian VXR-200 and JEOL GX-400 Fourier Transform NMR Spectrometers in $CDCl_3$ with Me_4Si as an internal standard. Infrared spectra were obtained on a Hitachi EPI-S2 IR Spectrometer. Elemental analyses were performed with a Yanako MT-3 Elemental Analyzer.

Materials

Tetrahydrofuran and toluene were distilled over sodium benzophenone ketyl prior to use. A hexane solution of butyllithium and hexamethylphosphoramide was obtained from a commercial source. Methyl 2-pyridylmethyl sulfoxide ($\mathbf{1_{2N}}$) *t*-butyl 2-pyridylmethyl sulfoxide ($\mathbf{2_{2N}}$) and *t*-butyl 4-pyridylmethyl sulfoxide ($\mathbf{2_{4N}}$) were prepared according to the literature procedure [18].

$\mathbf{1_{2N}}$: ^{1}H NMR (δ, $CDCl_3$) 2.58 (s, 3H), 4.12 (d, J = 13 Hz, 1H), 4.20 (d, J = 13 Hz, 1H), 7.25–7.78 (m, 3H), and 8.59–8.62 (m, 1H). $[\alpha]_D^{24}$ −70.6° (c 1.00, acetone) [19]

$\mathbf{2_{2N}}$: ^{1}H NMR (δ, $CDCl_3$) 1.34 (s, 9H), 3.77 (d, J = 13 Hz, 1H), 4.04 (d, J = 13 Hz, 1H), 7.20–7.72 (m, 3H), and 8.59–8.62 (m, 1H). $[\alpha]_D^{24}$ +303° (c 1.12, acetone); Ref. [18] $[\alpha]_D^{24}$ +304 (acetone).

$\mathbf{2_{4N}}$: ^{1}H NMR (δ, $CDCl_3$) 1.33 (s, 9H), 3.57 (d, J = 13 Hz, 1H), 3.75 (d, J = 13 Hz, 1H), 7.28 (d, J = 6Hz, 2H), and 8.59 (d, J = 6Hz, 2H). Anal calcd for $C_{10}H_{15}NOS$: C, 60.88; H, 7.66; N, 7.10%. Found: C, 60.59; H, 7.68; N, 6.98%.

Synthesis of Methyl (R)-1-(2-Pyridyl)ethyl Sulfide, t-Butyl (R)-1-(2-Pyridyl)-ethyl Sulfide and t-Butyl (R)-1-(4-Pyridyl)ethyl Sulfide

In a 50 ml round-bottomed flask, 341 mg (8.0 mmol) of sodium hydride (*ca.* 60% purity) and 30 mL of diethyl ether were placed under an argon atmosphere. The mixture was cooled to 0°C and stirred. Therein, 987 mg (8.0 mmol) of (*S*)-(−)-1-(2-pyridyl)ethanol which was prepared according to the literature procedure [20,21] ($[\alpha]_D^{24}$ −62.0° (c 2.50, EtOH): 98% optical purity) was added through a syringe. The mixture was stirred for 3 hour at room temperature. Then, 1.53 g (8.0 mmol) of *p*-toluenesulfonyl chloride in 10 mL of diethyl ether was added to the reaction mixture through a syringe. The mixture was then filtered, and the filtrate was evaporated under reduced pressure to afford the corresponding crude tosylate, which was subjected

to column chromatography on silica gel with ethyl acetate as an eluent to isolate 1.66 g (75% yield) of the pure tosylate. 158 mg (1.0 mmol) of methyl mercaptan (30% in MeOH) at 0°C were added to a stirred solution of sodium ethoxide prepared from 23 mg (1.0 mmol) of sodium metal in 10 mL of ethanol, then 277 mg (1.0 mmol) of the tosylate was added to this mixture. The mixture was stirred for 1 hour, while the temperature was allowed to rise to room temperature. After evaporation of the solvent under reduced pressure, the residue was subjected to column chromatography on silica gel with hexane/EtOAc (8/2) as an eluent to afford 94.8 mg of methyl (*R*)1-(2-pyridyl)ethyl sulfide (**4**) as a colorless liquid in 62% yield.

4: ^{1}H NMR (δ, $CDCl_3$) 1.63 (d, J = 7 Hz, 3H), 1.97 (s, 3H), 4.00 (q, J = 7 Hz, 1H), 7.13–7.70 (m, 3H), and 8.53–8.55 (m, 1H). $[\alpha]_D^{24}$ + 109.7° (c 1.27, $CHCl_3$). Anal calcd for $C_8H_{11}NS$: C, 62.70; H, 7.24; N, 9.14%. Found: C, 62.85; H, 7.32; N, 9.12%.

The same procedure was employed for the synthesis of *t*-butyl (*R*)-1-(2-pyridyl)ethyl sulfide (**5**) by the reaction of the corresponding tosylate with *t*-butyl mercaptan.

5: ^{1}H NMR (δ, $CDCl_3$) 1.21 (s, 9H), 1.58 (d, J = 7 Hz, 3H), 4.17 (q, J = 7 Hz, 1H), 7.08–7.68 (m, 3H), and 8.47–8.50 (m, 1H). $[\alpha]_D^{24}$ +225.4° (c 1.80, $CHCl_3$). Anal calcd for $C_{11}H_{17}NS$: C, 67.64; H, 8.77; N, 7.17%. Found: C, 67.57; H, 8.74; N, 7.04%.

General Procedure for the Methylation and Deuteronation of Sulfoxides

One mmol of a sulfoxide and 14 mL of THF were placed into a 20 mL flask under an argon atmosphere. The mixture was cooled to −78°C and stirred. A solution of butyllithium in hexane (0.63 mL, 1.1 mmol) was added to this mixture through a syringe. The mixture was kept at −78°C for an additional 20 minutes. The resulting solution was mixed with excess methyl iodide (or DCl/D_2O) and allowed to stand for 15 minutes. Saturated aqueous sodium chloride was added to the reaction mixture, and the total mixture was further stirred for a while without cooling. Then, the organic portion was repeatedly extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate, and the solvent was evaporated under reduced pressure. The ratio of unreacted H_S and H_R in the substituted product was determined by ^{1}H NMR analysis of the crude reaction product by observing the intensities of the signals from these protons. The chemical yield was also determined by ^{1}H NMR analysis using 1,1-diphenylethylene as an internal standard.

Determination of Absolute Configurations of the Methylated Sulfoxides

The sulfoxides isolated from the reaction mixture were reduced to the corresponding sulfides, and their absolute configurations at the α-sulfinyl carbon were determined by comparing their optical rotations with those of the corresponding authentic samples prepared, as described previously: the methyl 1-(2-pyridyl)ethyl sulfoxide was reduced by a $LiAlH_4/TiCl_4$ system to afford **4** of $[\alpha]_D^{24}$ −82.5° (c 1.39, $CHCl_3$) [19,22], and the 1-(2-pyridyl)ethyl *t*-butyl sulfoxide was reduced by a $PPh_3/NaI/I_2$ system to afford **5** of $[\alpha]_D^{24}$ + 220.2° (c 0.20, $CHCl_3$) [23]. The stereochemistry of the major isomer in the *t*-butyl 1-(4-pyridyl)ethyl sulfoxide ($\mathbf{2_{4N}}$) was determined with the aid of the ^{1}H NMR aromatic solvent-induced shift (ASIS) method with the references of those of $\mathbf{2_C}$ and $\mathbf{2_{2N}}$ [24]. The ASIS [$\delta(CCl_4)$-δ(benzene)] values which were obtained relative to TMS were +0.40 (for C**H**) and +0.18 (for C$\mathbf{H_3}$) for the major isomer and +0.50 (C**H**) and +0.40 (C$\mathbf{H_3}$) for the minor isomer.

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REFERENCES

[1] A. Rauk, S. Wolfe, I. G. Csizmadia, *Can. J. Chem., 47*, 1968, 113.
[2] K. Nishihata, M. Nishio, *J. Chem. Soc., Perkin Trans. II*, 1972, 1730.
[3] R. Viau, T. Durst, *J. Am. Chem. Soc., 95*, 1973, 1346.
[4] J. F. Biellmann, J. F. Blanzat, J. J. Vicens, *J. Am. Chem. Soc., 102*, 1980, 2460.
[5] N. Furukawa, E. Hosono, H. Fujihara, S. Ogawa, *Bull. Chem. Soc. Jpn., 63*, 1990, 461.
[6] For a review, see G. Solladié, *Synthesis*, 1981, 185.
[7] K. Nakamura, M. Higaki, S. Adachi, S. Oka, A. Ohno, *J. Org. Chem., 52*, 1987, 1414.
[8] M. Higaki, M. Goto, A. Ohno, *Heteroatom Chem., 1*, 1990, 181.
[9] K. Nishihata: Ph.D. Thesis, Kyushu University, 1975.
[10] G. Chassaing, A. Marquet, *Tetrahedron, 34*, 1978, 1399.
[11] G. Chassaing, A. Marquet, *J. Organomet. Chem., 232*, 1982, 293.
[12] A. Ohno, M. Higaki, S. Oka, *Bull. Chem. Soc. Jpn., 61*, 1988, 1721.
[13] M. Marsch, W. Massa, K. Harms, G. Baum, G. Boche, *Angew. Chem., Int. Ed. Engl., 25*, 1986, 1011.
[14] For a review, see G. Boche, *Angew. Chem., Int. Ed. Engl., 28*, 1989, 277.
[15] T. Durst, R. Viau, M. R. McClory, *J. Am. Chem. Soc., 93*, 1971, 3077.
[16] E. M. Arnett, M. A. Nichols, A. T. McPhail, *J. Am. Chem. Soc., 112*, 1990, 7059.
[17] E. M. Arnet, F. J. Fisher, M. A. Nichols, A. A. Ribeiro, *J. Am. Chem. Soc., 112*, 1990, 801.
[18] K.-U. Baldenius, H. B. Kagan, *Tetrahedron: Asymmetry, 1*, 1990, 597.
[19] The sulfinate which was used for the synthesis of $\mathbf{1_{2N}}$ had 100% optical purity: F. Rebiere and H. B. Kagan, *Tetrahedron Lett., 30*, 1989, 3659.

[20] J. Hermolin, J. Kopilov, E. Gileadi, *Electroanal. Chem., 71*, 1976, 245.
[21] M. Imuta, H. Ziffer, *J. Org. Chem., 43*, 1978, 3530.
[22] J. Drabowicz, M. Mikolajczyk, *Synthesis*, 1976, 527.
[23] G. A. Olah, B. G. B. Gupta, S. C. Narang, *Synthesis*, 1978, 137.
[24] Y. Kodama, K. Nishihata, M. Nishio, Y. Iitaka, *J. Chem. Soc., Perkin Trans. II*, 1976, 1490. The method is based on the assumption that the predominant conformer of *t*-butyl 1-(4-pyridyl)ethyl sulfoxide in solution resembles that in *t*-butyl 1-phenylethyl sulfoxide solution.