

# Novel Approach to the Synthesis of Enantioenriched Sulfoxides. Highly Diastereoselective Alkylation of Sulfenate Anions with 1,4-Asymmetric Induction

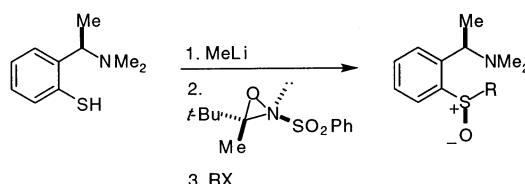
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## ABSTRACT



Efficient 1,4-asymmetric induction with an enantiopure aminoalkyl group as the chiral auxiliary has been achieved in the first example of diastereoselective alkylation (up to 98:2) of a sulfenate anion, readily prepared by oxidation of the corresponding thiolate. The stereochemistry of the sulfoxide produced is the opposite of that obtained by the conventional route based on oxidation of the sulfide precursor.

Sulfenate anions ( $\text{RSO}^-$ ) have been postulated as intermediates in various reactions involving sulfenate derivatives,<sup>1</sup> sulfoxides,<sup>2</sup> or sulfines<sup>3</sup> as substrates. However, no general

procedures for their preparation have so far been reported. In some recent studies of the oxidation of thiolates ( $\text{RS}^-$ ) with *N*-sulfonyloxaziridines,<sup>4</sup> we showed that aromatic lithium sulfenates could be obtained very efficiently using the unusual<sup>5</sup> ( $\pm$ )-*trans*-3-(1,1-dimethylethyl)-3-methyl-2-(phenylsulfonyl)oxaziridine **1** derived from pinacolone (Scheme 1). In situ *S*-alkylation of sulfenate anions with aliphatic halides afforded the corresponding sulfoxides in good to excellent yield. The overall sequence (deprotonation, oxidation, and alkylation) constitutes an original and effective approach to the synthesis of sulfoxides from thiols and has the considerable advantage of being carried out in one pot.

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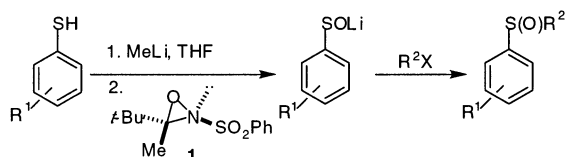
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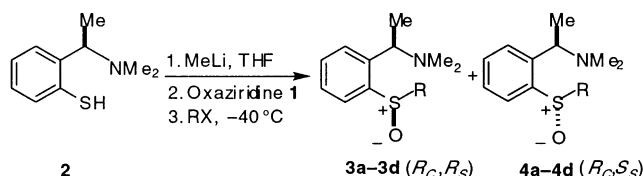
(5) With the exception of our work, there is only one reported example of the use of oxaziridine **1** (hydroxylation of a  $\beta$ -lactam). Shimizu, M.; Ishida, T.; Fujisawa, T. *Chem. Lett.* **1994**, 1403–1406.

Scheme 1



In this Letter we wish to describe an asymmetric version of this methodology, starting from enantiopure thiophenol **2** (Scheme 2). Since the substrate in this case possesses a

Scheme 2



stereogenic center, we anticipated a transfer of chirality during alkylation of the prochiral sulfenate and hence the preferential formation of one of the possible sulfoxide diastereoisomers. No examples of such diastereoselectivity have been reported up to now,<sup>6</sup> this being largely due to the previously mentioned lack of efficient methods for the generation of sulfenates. In contrast, diastereocontrolled syntheses of sulfoxides by oxidation of the corresponding chiral thioethers are well-documented.<sup>7</sup>

Our decision to pursue these investigations was for the following reasons: (i) The starting thiol **2** is reported to be readily available<sup>8</sup> from enantiopure ( $\alpha$ )-phenylethylamine, which is an inexpensive chiral amine sold as either enantiomer. (ii) Dialkylaminoethyl groups are known<sup>9</sup> to be efficient chiral auxiliaries. (iii) The products formed, which contain both amino and sulfoxide functions, are potentially useful chiral starting materials<sup>10</sup> for asymmetric synthesis or ligands<sup>11</sup> for catalysis.

(6) The sole example involving sulfenate salts in asymmetric synthesis concerns enantioselective alkylation with enantiopure sulfonium salts. Kobayashi, M.; Manabe, K.; Umemura, K.; Matsuyama, H. *Sulfur Lett.* **1987**, *6*, 19–24.

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(8) These thiols and related structures have been successfully used as chiral ligands for the catalytic asymmetric addition of dialkylzinc to aldehydes and in the substitution reaction of Grignard reagents with allylic acetates. (a) Kleijn, H.; Jastrzebski, J. T. B. H.; Boersma, J.; van Koten, G. *Tetrahedron Lett.* **2001**, *42*, 3933–3937. (b) Kleijn, H.; Rijnberg, E.; Jastrzebski, J. T. B. H.; van Koten, G. *Org. Lett.* **1999**, *1*, 853–855. (c) Wipf, P.; Ribe, S. *J. Org. Chem.* **1998**, *63*, 6454–6455. (d) Karlström, A. S. E.; Huerta, F. F.; Meuzelaar, G. J.; Bäckvall, J.-E. *Synlett* **2001**, SI, 923–926. (e) Meuzelaar, G. J.; Karlström, A. S. E.; van Klaveren, M.; Persson, E. S. M.; del Villar, A.; van Koten, G.; Bäckvall, J.-E. *Tetrahedron* **2000**, *56*, 2895–2903.

The influence of various parameters (temperature, addition of salts or crown ethers, nature of the electrophile) was examined. In addition, the stereochemistry was compared with that obtained using the more traditional route to sulfoxides through the oxidation of the sulfide precursors.<sup>7b</sup>

Enantiopure thiophenol **2** was prepared from 1-(*R*)-phenylethylamine. The first step, synthesis of tertiary amine, was achieved in 73% yield by Eschweiler–Clark methylation.<sup>12</sup> The subsequent conversion into the thiol using the methodology of van Koten et al.<sup>13</sup> comprises ortho-lithiation in pentane and isolation of the resulting carbanion by centrifugation, followed by trapping with elemental sulfur in THF, acidic workup, and purification by sublimation under reduced pressure. In our hands, however, this sequence gave only poor yields (<19%) under the literature conditions. The protonation of the intermediate thiolate was found to be particularly critical and highly dependent on the nature of the proton source. Optimum results were ultimately obtained using a stoichiometric amount of glacial acetic acid in THF, which afforded the dimethylamino thiol **2** in 65% yield.<sup>14</sup> This reaction was carried out on a 17 mmol scale, allowing the preparation of 2 g of product in one batch. Moreover, isolation of the ortho-metalated species was found to be unnecessary; the solution of the carbanion in pentane was added directly to the suspension of sulfur in THF.

The sequence (deprotonation, oxidation, and alkylation) was then applied to thiophenol **2**, using methyl iodide (1 equiv) as an initial electrophile, and the influence of various parameters (temperature, auxiliary reagents) was examined. Because of the low solubility of compound **2** at low temperature in THF, the deprotonation with methyllithium was carried out with warming from  $-78$  to  $-10$  °C, at which temperature complete solubilization was observed. After recooling to  $-78$  °C, oxidation of the thiolate was carried out<sup>15</sup> by addition of 1.05 equiv of *N*-sulfonyloxaziridine **1**. The alkylation was likewise performed at low temperature

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(10) Use of these substrates has previously been reported in the synthesis of two naturally occurring compounds. (a) Shimazaki, M.; Ohta, A. *Synthesis* **1992**, 957–958. (b) Shimazaki, M.; Ichihara, N.; Goto, M.; Ohta, A. *Chem. Pharm. Bull.* **1992**, *40*, 3072–3075.

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(13) Knotter, D. M.; van Maanen, H. L.; Grove, D. M.; Spek, A. L.; van Koten, G. *Inorg. Chem.* **1991**, *30*, 3309–3317.

(14) Disulfide can be easily removed by washing with diethyl ether. Compound **2** was obtained in 33% yield through addition of a stoichiometric amount of *p*-TsOH, whereas no thiol at all was isolated with methanolic HCl.

**Table 1.** Sulfenate Alkylation with Methyl Iodide According to Scheme 2

entry	<i>T</i> °C	time (h)	additives (equiv)	<b>3a:4a</b>	yield (%)
1	−40	24	none	84:16 <sup>a</sup>	70
2	−78	48	none	85:15	82
3	−40	36	LiBr (1)	83:17	89
4	−40	36	LiBr (5)	83:17	83
5	−40	36	12-crown-4 (1)	80:20	80

<sup>a</sup> These conditions were also employed in the corresponding reaction with the piperidinyll analogue [2-(CH<sub>2</sub>)<sub>4</sub>NCH(Me)C<sub>6</sub>H<sub>4</sub>SH], affording the methyl sulfoxides in 83% isolated yield and with a diastereomeric ratio of 84:16 (see ref 17).

to minimize the competitive N-alkylation and consequent formation of a water-soluble quaternary ammonium salt.<sup>16</sup> A lengthy reaction time of one or more days was allowed to efficiently trap the intermediate sulfenate.

Good diastereoselectivities were observed under all conditions tested (Table 1).<sup>18</sup> The alkylation of the lithium sulfenate proceeded with the predominant formation of the (*R<sub>c</sub>*,*R<sub>s</sub>*)-diastereoisomer **3a**.<sup>7b</sup> A diastereomeric ratio of 84:16 was obtained when the alkylation was performed at −40 °C (entry 1), with no increase in diastereoselectivity at lower temperature (−78 °C; entry 2). Addition of varying amounts of lithium bromide<sup>19</sup> to break up possible intermediate aggregate species had no significant effect (entries 3 and 4). The addition of 12-crown-4-ether to trap the lithium counterion and prevent internal chelations was also examined<sup>20</sup> but had negligible effect on the diastereomeric ratio observed (80:20; entry 5). Isolated yields were thus fairly consistent across a range of conditions, varying from 70% to 89%. Diastereomeric sulfoxides **3a** and **4a** were easily separated by column chromatography on silica gel, and their enantiomeric purity was checked by HPLC (see Supporting Information). This was greater than 99%, indicating that no epimerization had taken place in respect to the commercial 1-(*R*)-phenylethylamine.

(15) The oxidation is completely chemoselective at sulfur. No *N*-oxidation byproducts were detected in the final reaction mixture.

(16) On stirring (1*R*)-*N,N*-dimethyl-1-phenylethylamine with methyl iodide at room temperature in THF, precipitation occurred rapidly. The solid product was identified as the ammonium salt and was isolated in quantitative yield after a reaction time of 2 h.

(17) For the preparation of the piperidinyll thiol, see: (a) Tsuge, H.; Okano, T.; Eguchi, S.; Kimoto, H. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1581–1586. (b) Rijnberg, E.; Hovestad, N. J.; Kleij, A. W.; Jastrzebski, J. T. B. H.; Boersma, J.; Janssen, M. D.; Spek, A. L.; van Koten, G. *Organometallics* **1997**, 16, 2847–2857.

(18) The diastereomeric ratio was evaluated from the <sup>1</sup>H NMR of the crude mixture and was consistent with that of the purified product (±2%). The most diagnostically useful signals are those of the methine and methyl protons of the dimethylaminoethyl side chain.

(19) For examples in enolate chemistry, see: (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, 27, 1624–1654. (b) Henderson, K. W.; Dorigo, A. E.; Liu, Q.-Y.; Williard, P. G.; Schleyer, P. v. R.; Bernstein, P. R. *J. Am. Chem. Soc.* **1996**, 118, 1339–1347. (c) Asensio, G.; Aleman, P. A.; Domingo, L. R.; Medio-Simón, M. *Tetrahedron Lett.* **1998**, 39, 3277–3280. (d) Yanagisawa, A.; Kikuchi, T.; Yamamoto, H. *Synlett* **1998**, 174–176. (e) Murakata, M.; Yasukata, T.; Aoki, T.; Nakajima, M.; Koga, K. *Tetrahedron* **1998**, 54, 2449–2458. (f) Matsuo, J.-i.; Kobayashi, S.; Koga, K. *Tetrahedron Lett.* **1998**, 39, 9723–9726.

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**Table 2.** Sulfenate Alkylation with Various Alkyl Halides According to Scheme 2

entry	RX	time (h)	products (ratio)	yield (%)	oxidation ratio <sup>a</sup>
1	MeI	24	<b>3a:4a</b> (84:16)	70	11:89
2	EtI	48	<b>3b:4b</b> (84:16)	86	17:83
3	AllBr	48	<b>3c:4c</b> (81:19)	70 <sup>b</sup>	
4	BnBr	36	<b>3d:4d</b> (98:2)	43 <sup>c</sup>	40:60

<sup>a</sup> Oxidation with sodium perborate in glacial acetic acid (see ref 7b). <sup>b</sup> Crude yield. <sup>c</sup> The lower yield in this case is a consequence of substantial N-alkylation during workup owing to the presence of unreacted benzyl bromide, which is nonvolatile.

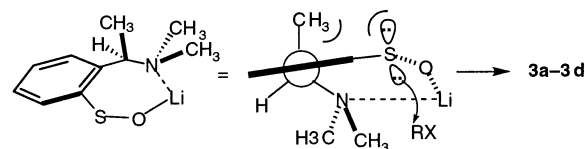
The same reaction was then investigated with various other electrophiles, including ethyl iodide and allyl and benzyl bromides. Once again, good to excellent diastereoselectivities were observed (Table 2). When quenching with ethyl iodide or allyl bromide, the diastereomeric distribution is similar to that obtained with methyl iodide (entries 1–3), though an excess of halide (3–5 equiv) is necessary to efficiently trap the sulfenate. The major products **3a** and **3b** were shown to have a (*R<sub>c</sub>*,*R<sub>s</sub>*) configuration by comparison with literature data.<sup>7b</sup> Interestingly, a single diastereoisomer was produced using benzyl bromide as the electrophile (entry 4), the X-ray structure of which confirmed the same (*R<sub>c</sub>*,*R<sub>s</sub>*) configuration (see Supporting Information). Separation of diastereoisomers **3** and **4** was straightforward, with the exception of the allyl sulfoxides, which decomposed upon attempted purification.

Remarkable differences in NMR data are observed for the pair of diastereoisomeric sulfoxides, the benzylic methine proton in **3** occurring some 0.7 ppm downfield of the corresponding proton in **4**, as has previously been reported by Ohta.<sup>7b</sup> An unambiguous configuration dependence was likewise observed in the <sup>13</sup>C NMR spectra for the benzylic methine and methyl signals. The methyl substituent occurs below 10 ppm in compound **3** but is substantially deshielded at δ 20 ppm in **4**, and the tertiary carbon has a chemical shift of 58 ppm in diastereoisomer **3**, compared with a value of 63 ppm in **4**.

This novel approach to the synthesis of chiral sulfoxides was compared with the alternative strategy based on oxidation of the corresponding aryl thioethers. This reaction, previously examined by Ohta<sup>7b</sup> with substrates containing methyl, ethyl, and benzylic substituents at sulfur, was found to show a dramatic dependence on the reaction conditions employed. The highest diastereoselectivities were achieved using sodium perborate in glacial AcOH as oxidant (Table 2), with the (*R<sub>c</sub>*,*S<sub>s</sub>*) configuration products predominantly obtained. This stereochemistry is the opposite to that observed using our sulfenate-based approach. With the methyl and ethyl sulfides, ratios of 11:89 and 17:83, respectively, in favor of diastereoisomers **4a** and **4b** were obtained, whereas the alkylation of the sulfenate gave a reversed diastereoselectivity of 84:16 (entries 1–2). A moderate diastereoselectivity of 40:60 was reported for the benzyl derivative (entry 4). In contrast, our methodology gave exclusively diastereoisomer **4d**. Since *N*-sulfonyloxaziridines

have not been tested<sup>21</sup> by Ohta, we decided to perform in this series the oxidation of the methyl sulfide<sup>22</sup> with compound **1**. This reaction, carried out in THF, led to the formation in 84% yield of sulfoxides **3a** and **4a** respectively in a 31:69 ratio.<sup>23</sup> Similar results were also obtained with dichloromethane or toluene as solvent. The diastereoselectivity is slightly lower than that reported with sodium perborate but is still in favor of compound **4a**.

To rationalize the asymmetric induction observed in the alkylation of the prochiral sulfenate, we suggest a model<sup>24</sup> combining steric factors and restricted conformation of the benzylic dimethylamino group through chelation of the nitrogen atom with the lithium counterion, as depicted in Figure 1. In such a conformation, the methyl group of the stereogenic center hinders the approach of the electrophile toward the upper sulfur lone pair. The other diastereotopic lone pair is more accessible and can thus react preferentially to give the (*R<sub>c</sub>*,*S<sub>s</sub>*)-diastereoisomer. Evidence pointing to a strong interaction between lithium and nitrogen is the very



**Figure 1.** Proposed model.

modest difference in diastereoselectivity observed in the presence of crown ether and the Li–N distance value<sup>25</sup> of 1.45 Å calculated using Spartan software.

In conclusion, we have described the very first diastereoselective alkylation of sulfenate ions to give sulfoxides. An efficient 1,4-asymmetric induction, with diastereomeric ratios of up to 98:2, was accomplished using an enantiopure dimethylaminoethyl group as the chiral auxiliary. One interesting feature of this method is that the major diastereoisomer formed is the opposite of that available via the sulfide oxidation route, thus affording two complementary approaches to sulfoxides from thiols. Further investigations into the use of sulfenates in asymmetric synthesis are underway.

**Acknowledgment.** We gratefully acknowledge financial support from the Ministère de l'Éducation Nationale de l'Enseignement Supérieur et de la Recherche (F.S.). We also thank Prof. Pierre Beslin for discussions.

**Supporting Information Available:** Experimental procedures and full spectroscopic data for thiophenol **2** and sulfoxides **3** and **4**. Details of the X-ray crystallographic analysis of benzyl sulfoxide **3d**. HPLC chromatogram for methyl sulfoxides **3a** and **4a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(25) Bond lengths of around 2 Å have previously been reported in sparteine-mediated reactions of lithium reagents: Hoppe, D.; Hense, T. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 2282–2316.

(21) The oxidizing agents tested were peracids, hydrogen peroxide, potassium persulfate, and sodium perborate.

(22) The methyl sulfide was prepared in 86% yield from (1*R*)-*N,N*-dimethyl-1-phenylethylamine by ortho-lithiation and trapping with dimethyl disulfide (see ref 7b).

(23) In contrast, oxidation with the more classical benzaldehyde-derived oxaziridine, namely, (±)-*trans*-2-(phenylsulfonyl)-3-phenyloxaziridine, gave a complex mixture in which sulfoxides **3a** and **4a** could be detected (yield < 40%). Among the side products, 1-methylsulfonyl-2-vinylbenzene was produced in 28% yield, with spectral data in agreement with those reported: Bianchini, C.; Frediani, P.; Herrera, V.; Jiménez, M. V.; Meli, A.; Rincón, L.; Sánchez-Delgado, R.; Vizza, F. *J. Am. Chem. Soc.* **1995**, 117, 4333–4346. The formation of this styrene derivative can be interpreted in terms of a competitive oxidation on nitrogen followed by Cope elimination and illustrates the difference of oxidizing power of the two oxaziridines. For precedents, see: Christian, P. W. N.; Gibson (née Thomas), S. E.; Gil, R.; Jones, C. V.; Marcos, C. F.; Precht, F.; Wierzchlejski, A. T. *Recl. Trav. Chim. Pays-Bas* **1995**, 114, 195–202. For a review of the use of this oxaziridine, see: Davis, F. A.; Sheppard, A. C. *Tetrahedron* **1989**, 45, 5703–5742.

(24) No X-ray crystallographic structural data for sulfenate salts has been reported in the literature. However, we believe that lithium is coordinated to oxygen rather than to sulfur, on the basis of the accepted concepts of hard and soft acids and bases: Pearson, R. G. *Hard and Soft Acids and Bases*; Sisler, H. H., Ed.; Dowden, Hutchinson and Ross: Stroudsburg, 1973.