Preparation, Properties, and Chemical Reactivity of α-Nitrosulfoximines, Chiral Analogues of α-Nitrosulfones

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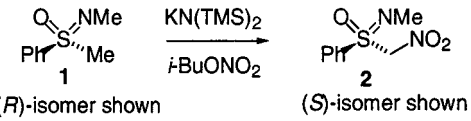
Racemic *N*-methyl-*S*-(nitromethyl)-*S*-phenylsulfoximine (**2**) was prepared in 87% yield via alkaline nitration of *N,S*-dimethyl-*S*-phenylsulfoximine. Optically active *N*-methyl-*S*-(nitromethyl)-*S*-phenylsulfoximine (both enantiomers) was prepared in similar fashion. Reaction of racemic **2** with *p*-chlorophenyl isocyanate and a catalytic quantity of triethylamine in the presence of furan afforded dihydrofuroisoxazole **5**, the product of nitrile oxide cycloaddition, in 42% yield (65:35 diastereomer ratio). Reaction of the dihydrofuroisoxazole **5** with phenyllithium and methyllithium afforded replacement of the sulfoximine group by phenyl and methyl, respectively. Reaction of racemic **2** with aromatic isocyanates and potassium carbonate afforded *C*-acylation products in 70−78% yield which existed as the ylide tautomers **9a,b**. Methylation of racemic **2** afforded the *C*-alkylate *N*-methyl-*S*-(1-nitroethyl)-*S*-phenylsulfoximine (**13**), existing as the neutral tautomer.

α-Nitrosulfoximines, chiral analogues of α-nitrosulfones, have never been reported in the literature. Here we report the synthesis, properties, and chemical reactivity of several members of this new class of compounds.

Racemic *N,S*-dimethyl-*S*-phenylsulfoximine (**1**), available via the procedure of Johnson et al.,[1] underwent alkaline nitration to afford *N*-methyl-*S*-(nitromethyl)-*S*-phenylsulfoximine (**2**), the parent α-nitrosulfoximine. Our initial studies employed butyllithium and LDA as bases with commercially available isobutyl nitrate as the nitrating agent. α-Nitrosulfoximine **2** was obtained under these conditions but only in 10−20% yield.



Truce and Feuer et al.[2] have reported the similar alkaline nitration of sulfones. They attributed higher yields to avoidance of overly strong bases and suggested a possible preference for the potassium rather than lithium counterion. We were gratified to obtain α-nitrosulfoximine **2** in 87% yield using commercially available potassium hexamethyldisilamide (KHMDS) rather than LDA or butyllithium as the base. In similar fashion, alkaline nitration of (*R*)-(−)-**1** afforded (*S*)-(+)-*N*-methyl-*S*-(nitromethyl)-*S*-phenylsulfoximine (**2**) and alkaline nitration of (*S*)-(+)-**1** afforded (*R*)-(−)-**2**. Optically pure samples of the starting sulfoximine **1** were prepared by the excellent procedure of Brandt and Gais.[3]

Sulfoximines as a class are known to be basic, the imine N-atom undergoing protonation and also methylation.[1] The α-nitrosulfoximine **2** is also relatively acidic: its first pK_a, measured in 50:50 methanol/water, was 6.3. Thus, α-nitrosulfoximine **2** is an amphoteric compound.

The proton NMR spectra of α-nitrosulfoximine **2** were strongly reminiscent of alcohol spectra (Figure 1). Like the O−H proton of an alcohol, the diastereotopic methylene protons of α-nitrosulfoximine **2** showed a significant concentration dependence. In dilute (0.06 M) deuteriochloroform solution, **2** exhibited two sharp doublets at δ 5.70 and 5.60 (J = 11.1 Hz) attributed to the methylene protons. In more concentrated solution (3.5 M), both signals occurred at lower field (δ 5.83 and 5.76, respectively) with little or no apparent broadening or change in the coupling constant. However, impure samples of **2** did show appreciable line broadening of the methylene proton signals. Furthermore, the methylene protons of **2** underwent relatively rapid exchange (<2 min) at pH 7 when a deuteriochloroform solution of **2** was brought into contact with deuterium oxide. In contrast, the more acidic (phenylsulfonyl)nitromethane (pK_a 5.7[4]), which lacks a basic site, did not undergo appreciable exchange under these conditions.

The diastereotopic methylene protons of α-nitrosulfoximine **2** also showed clear indication of rapid exchange under both acidic and basic conditions. In the presence of a trace of acetic acid, line broadening and partial coalescence of the methylene proton signals were observed. Formation of an iminium ion and subsequent formation of the transient ylide **3** from the imminium ion would explain these observations (Scheme 1). The effect of a small amount of triethylamine on **2** was even more pronounced than the effect of acid: line broadening was more severe for the same quantity of catalyst. Here equilibration must have occurred via formation and reprotonation of the nitronate.

Our original interest in preparing **2** was its potential for conversion to a chiral nitrile oxide analogous to achiral (phenylsulfonyl)carbonitrile oxide[5] (Scheme 2). It has previously been shown that (phenylsulfonyl)carbonitrile oxide is an effective 1,3-dipole undergoing cycloaddition to a wide variety of alkenes, even alkenes that are

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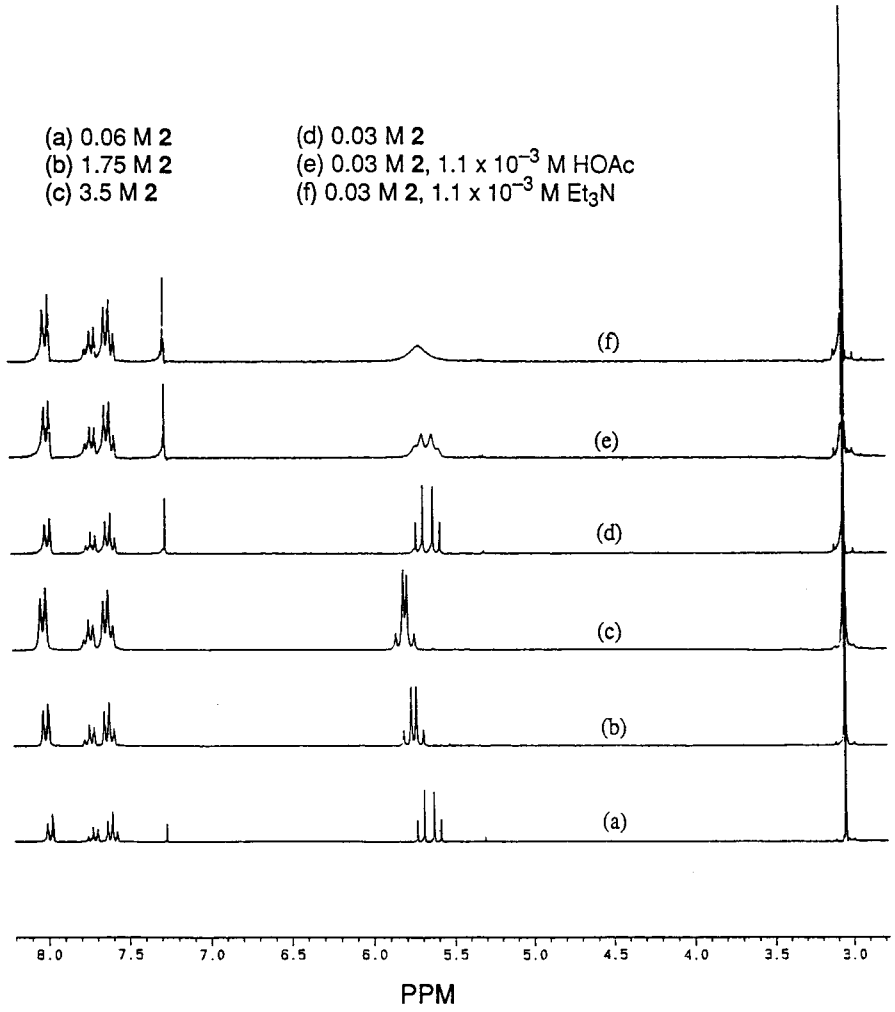
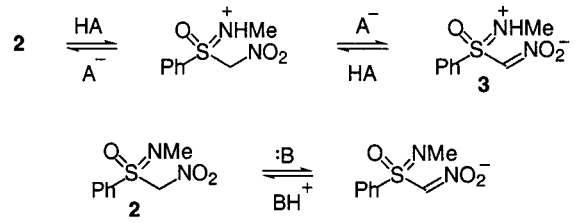


Figure 1. Stacked ^{1}H NMR spectra of α-nitrosulfoximine **2**.

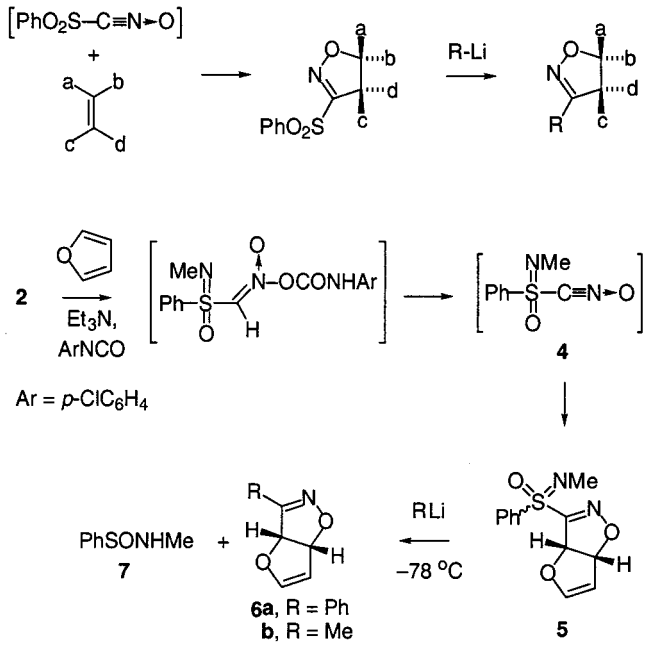
Scheme 1



sluggish in reaction with other nitrile oxides.[5] Furthermore, the sulfone group present in the resulting dihydroisoxazoles can be readily replaced by nucleophiles, thus affording a general synthesis of dihydroisoxazoles from a single nitrile oxide precursor.[6]

It was anticipated that a general asymmetric synthesis of dihydroisoxazoles based on optically active **2** might be possible. This matter has been tested with racemic **2** pursuant to the development of an actual asymmetric synthesis. Furan, a well-known sluggish dipolarophile, was chosen as the olefinic component for examination. Warming a solution of racemic **2**, *p*-chlorophenyl isocyanate, furan, and a catalytic quantity of triethylamine in chloroform did indeed afford a 42% yield of the nitrile oxide cycloaddition product dihydrofuroisoxazole **5**. Ster-

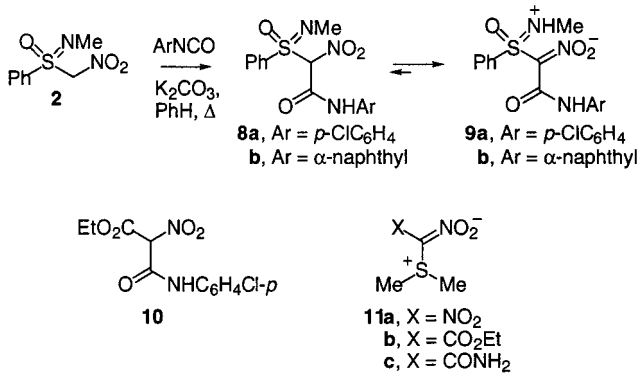
Scheme 2



eochemical induction was moderate: a mixture of diastereomers (65:35 isomer ratio, major isomer not determined) was obtained. These diastereomers could be partially separated into enriched fractions by thin-layer

(6) Wade, P. A.; Yen, H.-K.; Hardinger, S. A.; Pillay, M. K.; Vail, P. D.; Morrow, S. D. *J. Org. Chem.* **1983**, *48*, 1796.

Scheme 3



chromatography, but complete separation has not yet been obtained.

There can be little doubt that nitrile oxide **4**, the first sulfoximinyl nitrile oxide, was an intermediate in the formation of dihydrofuroisoxazole **5**. Apparently, *O*-acylation of **2** occurred followed by elimination. However, if more than a catalytic amount of triethylamine was employed, there was a competing side reaction. For example, in the presence of 0.25 molar equiv of triethylamine, ylide **9a** was obtained in 20% yield (Scheme 3). Apparently **9a** was derived from *C*-acylation of the anion of **2** and ensuing tautomerization.

To complete the initial test of the generality of dihydroisoxazole synthesis using nitrosulfoximine **2**, the replacement of the sulfoximine group was investigated. Reaction of **5** with phenyllithium in THF at −78 °C afforded the dihydrofuroisoxazole **6a** in 48% yield as well as the sulfinamide **7**[7] as a byproduct. Similarly, reaction of **5** with methyllithium afforded **6b** in 54% yield.

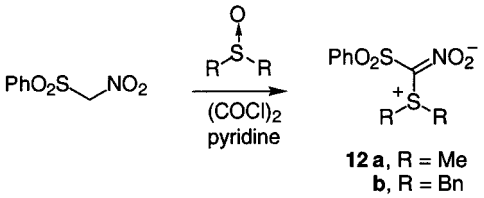
Thus, the initial test demonstrates that **2** is capable of affording the sulfoximinyl nitrile oxide and cycloadducts derived from it. If optically active **2** were used, the cycloadducts that would be formed should be nonracemic diastereomers. Furthermore, the sulfoximine group can be readily replaced to provide dihydroisoxazoles with an alkyl or aryl group on the C-atom of the *C*,*N*-double bond. Elaboration of these initial results is still required: improved cycloaddition procedures with a higher stereoselectivity and better overall yield need to be developed and applied to the optically active nitrile oxide precursor.

The formation of the novel ylide **9a** has been further investigated. Heating a benzene solution of α-nitrosulfoximine **2** and *p*-chlorophenyl isocyanate in the presence of solid potassium carbonate afforded **9a** in 78% yield. α-Nitrosulfoximine **2** also underwent reaction with α-naphthyl isocyanate under similar conditions to afford ylide **9b** in 70% yield.

There is a literature report[8] concerning the *C*-acylation of ethyl nitroacetate by *p*-chlorophenyl isocyanate. The resulting product is the neutral *C*-acylate, nitro ester **10**, and not the ylide tautomer. However, the ylide tautomers **9a,b** rather than the neutral tautomers **8a,b** were clearly formed from *C*-acylation of **2**. The ^{1}H NMR spectrum of **9a** showed coupling between the *N*-methyl group and the N−H (located at δ 12.04). The ^{13}C NMR spectrum of **9a** exhibited a signal at δ 112.3 attributed to the nitronate C-atom. Infrared spectra showed asymmetric and symmetric NO_2 stretching bands (ν_{as} 1425 cm^{-1} and ν_s 1327 cm^{-1}) characteristic of a nitronate rather than a nitro group.

It seems unusual for the zwitterionic ylide tautomers **9a,b** to be favored over the neutral tautomers **8a,b**. Formation of the ylide tautomers **9a,b** might well be driven by intramolecular H-bonding. Perhaps H-bonding from the amide proton to one nitronate O-atom and from the iminium proton to the other nitronate O-atom occurs, resulting in stabilization of the ylide tautomer. Such double stabilization of nitronates has a precedent.[9]

The nitro group is especially capable of stabilizing adjacent carbanions. Thus, there are a number of known stable nontautomerizable ylides (e.g., **11a**−**c**) involving sulfonium cations adjacent to nitronate centers.[10] It was desired to prepare examples of this class for comparison to ylides **9a,b**. Consequently, the previously unreported ylides **12a,b** were synthesized from (phenylsulfonyl)-nitromethane using oxalyl chloride under Swern[11] conditions.



Spectra of the ylides **12a,b** resembled the reported spectra of ylides **11a**−**c**.[10] Infrared bands for the nitronate group of **12a** (ν_{as} 1403 cm^{-1} and ν_s 1273 cm^{-1}) and of **12b** (ν_{as} 1408 cm^{-1} and ν_s 1293 cm^{-1}) are consistent with similar values reported for ylides **11b** (ν_{as} 1385 cm^{-1} and ν_s 1279 cm^{-1}) and **11c** (ν_{as} 1412 cm^{-1} and ν_s 1290 cm^{-1}) as well as the α-nitrosulfoximine ylides **9a,b**. The ^{13}C NMR signals at δ 99.2 for **12a** and δ 99.6 for **12b** were attributed to the nitronate C-atoms, similar to the reported values for **11a**, **11b**, and **11c** (δ 121.5, 94.2, and 98.9, respectively) but at somewhat higher field than the nitronate C-atoms of **9a,b** (δ 112.3 and 112.5, respectively). Presumably the higher oxidation state of the sulfoximinium ion is responsible for the lower field chemical shift of **9a,b**.

After the observation of ylide tautomers **9a,b** as the products of *C*-acylation, the question of what products would be formed from alkylation was addressed. The methylation of α-nitrosulfoximine **2** occurred predominantly on the nitronate C-atom rather than the nitronate O-atom (Scheme 4). Thus, reaction of **2** in THF with KHMDS afforded the anion, which was methylated with excess methyl iodide. The crude product contained the neutral *C*-alkylate **13** as the major product (55:45 mixture of diastereomers), contaminated with a small amount of starting **2**. The starting material could not be separated by simple chromatography (TLC or column) but could be removed by making use of its higher kinetic acidity.[12] Unfortunately, some of the **13** (and likely also

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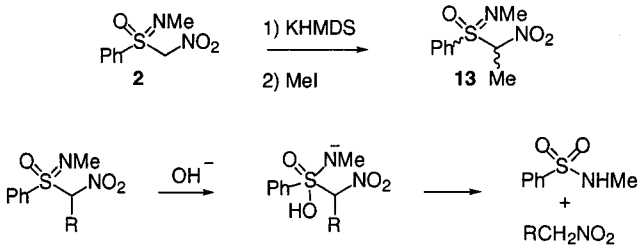
(11) Mancuso, A. J.; Swern, D. *Synthesis* **1981**, *3*, 165.

Scheme 4



2) underwent hydrolysis to *N*-methylbenzenesulfonamide during the extraction. The new contaminants were, however, readily removed by chromatography to afford pure **13**. It would seem that base readily attacks the S-atom of α-nitrosulfoximines with ensuing fragmentation. However, a catalytic quantity (5 mol %) of triethylamine neither destroyed nor racemized a sample of optically active α-nitrosulfoximine **2**. Chloroform solutions of optically active **2** also developed *N*-methylbenzenesulfonamide over time, indicative of slow acid-catalyzed hydrolysis.

Experimental Section

General Procedures. NMR spectra (250 MHz for ^{1}H in $CDCl_3$ unless otherwise noted) were obtained as previously described.[13] Microanalyses were performed at the microanalytical facility, Department of Chemistry, University of Pennsylvania. *N*,*S*-Dimethyl-*S*-phenylsulfoximine (**1**) was prepared from *S*-methyl-*S*-phenylsulfoximine according to the reported method of Johnson et al.[1] Resolution of racemic *S*-methyl-*S*-phenylsulfoximine was accomplished using the method of Brandt and Gais.[3] All reactions were run under nitrogen and were routinely worked up by extracting with CH_2Cl_2 (three 25 mL portions), washing of the combined organic layers with water (three 50 mL portions), drying over anhydrous Na_2SO_4, filtering, and concentrating under reduced pressure. Flash chromatography was carried out using 30 g portions of silica gel.

Preparation of (+)-*N*-Methyl-S-(nitromethyl)-*S*-phenylsulfoximine (2). A 0.5 M toluene solution of KHMDS (16.1 mL, 8.1 mmol of KHMDS) was added to a cold (dry ice) solution of (−)-sulfoximine **1** (0.54 g, 3.2 mmol) in THF (20 mL). The resulting solution was allowed to warm to −40 °C and was stirred for 30 min. A second solution containing isobutyl nitrate (1.3 mL, 10.8 mmol) in THF (5 mL) was then added dropwise over 1 h. The resulting solution was stirred for 6 h at −35 to −40 °C and was subsequently poured into aqueous 10% HOAc (100 mL). Workup afforded an oil which was purified by flash column chromatography (CH_2Cl_2 and then 99:1 CH_2Cl_2/MeOH elution) to give pure **2** (0.60 g, 87% yield) as an amber oil: $[\alpha]^{25}_D$ +32.73° (*c* 3.0, MeOH); $[\alpha]^{25}_D$ +53.07° (*c* 0.98, $CHCl_3$).

Prepared in a similar fashion was (−)-**2**: $[\alpha]^{25}_D$ −52.92° (*c* 0.98, $CHCl_3$).

Prepared in a similar fashion was (±)-**2**: IR (film) 1554 ($\nu_{as}(NO_2)$), 1358 ($\nu_s(NO_2)$), 1273 (ν_{as}(N=S=O)), and 1152 (ν_s(N=S=O)) cm^{-1}; ^{1}H NMR (0.06 M in $CDCl_3$) δ 7.56−8.00 (m, 5H), 5.70 (d, 1H, *J* = 11.1 Hz), 5.60 (d, 1H, *J* = 11.1 Hz), 3.04 (s, 3H); ^{13}C NMR δ 135.5, 134.4, 129.4, 129.1, 88.0, 29.4; MS (CI) *m*/*z* 215 [M + H] $^+$.

Anal. Calcd for $C_8H_{10}N_2O_3S$: C, 44.85; H, 4.70; N, 13.08. Found: C, 44.71; H, 4.90; N, 13.09.

Formation of Dihydrofuroisoxazole 5. A solution of 4-chlorophenyl isocyanate (0.35 g, 2.25 mmol) in furan (2 mL) was added dropwise over 5 min to a solution of (±)-α-nitrosulfoximine **2** (0.19 g, 0.90 mmol) and triethylamine (6 mL, 0.05 mmol) in furan (10 mL). The resulting stirred solution was heated at 40−45 °C for 2 d. The cooled (20 °C) solution was poured into 50 mL of aqueous 10% HOAc. Workup afforded the crude product which was purified by flash column chromatography (CH_2Cl_2/MeOH, 99:1) and subsequent preparative thin-layer chromatography (EtOAc/hexanes, 50:50) to give 0.10 g (42% yield) of **5** as an oil which was an otherwise pure 65:35 diastereomeric mixture: ^{1}H NMR δ 7.5−8.1 (m, 5H), 6.62 (dm, 1H min, *J* = 2.6 Hz), 6.47 (dm, 1H maj, *J* = 2.6 Hz), 6.0−6.1 (m, 2H), 5.37 (m, 1H min), 5.31 (dd, 1H maj, *J* = 1.3, 2.6 Hz), 3.00 (s, 3H maj), 2.96 (s, 3H min); HRMS (CI) *m*/*z* calcd for $C_{12}H_{13}N_2O_3S$ [M + H]$^+$ 265.0647, found 265.0655.

Further preparative thin-layer chromatography (CH_2Cl_2/MeOH, 98:2) afforded enriched fractions of the diastereomers: 70:30 (top half of the band) and 45:55 (bottom half of the band).

Conversion of Dihydrofuroisoxazole 5 to *cis*-3a,6a-Dihydro-3-phenylfuro[2,3-d]isoxazole (6a). A solution of PhLi (1.8 M in cyclohexanes/ether, 0.41 mL, 0.68 mmol) was added dropwise to a cold solution (−75 to −78 °C) of dihydrofuroisoxazole **5** (78 mg, 0.29 mmol) in THF (25 mL). The resulting cold solution was stirred for 30 min and poured into water, and 5% HCl (20 mL) was added. Further workup afforded the crude product which was purified by preparative thin-layer chromatography (EtOAc/hexanes, 20:80 elution) followed by a second preparative thin-layer chromatography (benzene elution) to afford 26 mg (48% yield) of **6a**, the more mobile fraction, as an oil. The spectra (^{1}H NMR, IR, ^{13}C NMR) matched reported spectra[14] for **6a**. The oil crystallized very slowly and only when pure: mp 44−46 °C (lit.[14b] mp 45−46 °C).

Conversion of Dihydrofuroisoxazole 5 to *cis*-3a,6a-Dihydro-3-methylfuro[2,3-d]isoxazole (6b). 6b was prepared in 54% yield similarly to **6a** using MeLi rather than PhLi and purification by preparative thin-layer chromatography (CH_2Cl_2/MeOH, 99:1 elution). The spectra (^{1}H NMR, IR, ^{13}C NMR) matched reported spectra[14a] except that the literature ^{1}H NMR value attributable to the methyl group (δ 1.3) was found to actually be δ 2.09, consistent with other related 3-methyl-4,5-dihydroisoxazoles (e.g., δ 1.98 for 5-butyl-3-methyl-4,5-dihydroisoxazole[15]). Also isolated was *N*-methylbenzenesulfinamide[16] (6.3 mg), obtained from the least mobile phase of the first chromatography.

Preparation of Ylide 9b. A stirred mixture containing α-nitrosulfoximine **2** (0.086 g, 0.40 mmol), 1-naphthyl isocyanate (0.068 g, 0.40 mmol), anhydrous K_2CO_3 (0.056 g, 0.40 mmol), and benzene (10 mL) was heated at reflux for 12 h. Solids were filtered from the cooled mixture and washed with CH_2Cl_2. The combined organic layers were further worked up, giving an oil which was purified by flash column chromatography to afford 0.14 g of crystals from the most mobile fractions. Recrystallization from EtOH afforded 0.11 g (70% yield) of **9b** as a yellow crystalline solid: mp 149−151 °C dec; IR (KBr) 3237 (N−H), 1619 (C=O) 1559 (amide II), 1418 (ν_{as}(nitronate)), and 1318 (ν_s(nitronate)) cm^{-1}; ^{1}H NMR δ 12.39 (br q, 1H, *J* = 4.8 Hz), 11.75 (br s, 1H), 7.5−8.1 (m, 12H), 2.69 (d, 3H, *J* = 4.8 Hz); ^{13}C NMR δ 161.1, 135.1, 134.4, 134.1, 131.8, 129.5, 129.4, 128.6, 127.5, 126.8, 126.3,126.2, 125.5, 121.4, 121.1, 112.5, 25.5; HRMS (M + Na$^+$) *m*/*z* calcd for $C_{19}H_{17}N_3O_4SNa$ 406.0837, found 406.0852.

Anal. Calcd for $C_{17}H_{17}N_3O_4S$: C, 59.52; H, 4.47; N, 10.96. Found: C, 59.72; H, 4.51; N, 10.90.

Preparation of Ylide 9a. Ylide **9a** was obtained in 78% yield following the procedure used for the preparation of **9b** except that *p*-chlorophenyl isocyanate replaced 1-naphthyl isocyanate: mp 149−149.5 °C; IR (KBr) 3259 (N−H), 1605 (C=O) 1513 (amide II), 1425 (ν_{as}(nitronate)), and 1327 (ν_s(ni-

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tronate)) cm^{-1}; ^1H NMR δ 12.04 (br q, 1H, J = 4.8 Hz), 11.25 (br s, 1H), 7.5−8.0 (m, 5H), 7.41 (dm, 2H, J = 8.8 Hz), 7.25 (dm, 2H, J = 8.8 Hz), 2.61 (d, 3H, J = 4.8 Hz); ^{13}C NMR δ 160.5, 135.4, 135.0, 134.5, 130.1, 129.5, 129.3, 129.1, 122.7, 112.3, 25.5; HRMS (FAB, M + H^+) m/z calcd for $C_{15}H_{15}N_3O_4S^{35}Cl$ 368.0472, found 368.0464.

Anal. Calcd for $C_{15}H_{14}N_3O_4SCl$: C, 48.98; H, 3.84; N, 11.42. Found: C, 49.03; H, 3.68; N, 11.48.

Preparation of Ylide 12a. A solution of anhydrous DMSO (1.1 mL, 15.24 mmol) in CH_2Cl_2 (12 mL) was added dropwise to a cold (dry ice) solution of 98% oxalyl chloride (0.44 mL, 5.08 mmol) in CH_2Cl_2 (12 mL). The resulting solution was allowed to stir for 1 min, and a solution of (phenylsulfonyl)-nitromethane (0.51 g, 2.54 mmol) and pyridine (0.51 mL, 6.35 mmol) in CH_2Cl_2 (12 mL) was added dropwise over a 15 min period. Stirring was continued for an additional 15 min, and the cold reaction solution was poured into ice/water (100 mL). Extraction with CH_2Cl_2 (three 25 mL portions) afforded a combined organic layer which was washed with 5% aqueous NaOH (100 mL). Further workup of the organic layer afforded a solid which was recrystallized from 95% EtOH to give 0.45 g (68% yield) of **12a** as colorless needles: mp 184−86 °C; IR (KBr) 1403 (ν_{as}(nitronate)),1333 ($\nu_{as}(SO_2)$), 1273 (ν_s(nitronate)), and 1142 ($\nu_s(SO_2)$) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.5−8.0 (m, 5H), 3.18 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 141.9, 132.8, 128.8, 127.5, 99.2, 27.5; MS (FAB) m/z (M + Na)$^+$ 284, (M + H)$^+$ 262.

Anal. Calcd for $C_9H_{11}NO_4S$: C, 41.38; H, 4.21; N, 5.36. Found: C, 41.31; H, 4.13; N, 5.31.

Preparation of Ylide 12b. 12b was prepared in 58% yield similarly to **12a** employing benzyl sulfoxide rather than DMSO: mp 170−72 °C; IR (KBr) 1408 (ν_{as}(nitronate)), 1312 ($\nu_{as}(SO_2)$), 1293 (ν_s(nitronate)), and 1137 ($\nu_s(SO_2)$) cm^{-1}; ^1H NMR (DMSO-d_6) δ 7.15−7.4 (m, 15H), 5.12 (d, 2H, J = 11.8 Hz), 4.51 (d, 2H, J = 11.8 Hz); ^{13}C NMR (DMSO-d_6) δ 146.5, 137.3, 135.6, 134.6, 134.5, 133.5, 132.3, 99.6, 50.9; MS (FAB) m/z (M + Na)$^+$ 436, (M + H)$^+$ 414.

Anal. Calcd for $C_{21}H_{19}NO_4S$: C, 60.79; H, 4.63. Found: C, 60.73; H, 4.30.

Preparation of (±)-*N*-Methyl-*S*-(1-nitroethyl)-*S*-phenylsulfoximine (13). A 0.5 M toluene solution of KHMDS (1.94 mL, 0.97 mmol of KHMDS) was added to a cold (dry ice) solution of (±)-α-nitrosulfoximine **2** (94 mg, 0.44 mmol) in THF (10 mL). The resulting solution was allowed to warm to −40 °C and was stirred for 5 min. A solution of iodomethane (75 mg, 0.53 mmol) in THF (1 mL) was added dropwise to the first solution over 5 min, and the resulting solution was stirred for 24 h at ambient temperature. The reaction solution was poured into 50 mL of aqueous 10% HCl, and the mixture was worked up to afford the crude product, containing a small portion of starting material **2**, which was dissolved in CH_2Cl_2 (50 mL). Rapid extraction with 5% aqueous $NaHCO_3$ (50 mL) removed most of the **2** that could be recovered by acidification of the aqueous layer with 5% HCl followed by further workup. The organic layer contained mostly **13**. Three iterations of this procedure as previously reported for 1-(phenylsulfonyl)-1-nitroethane[10] afforded 10 mg of recovered starting α-nitrosulfoximine **2** and **13** free of **2** but contaminated by *N*-methylbenzenesulfonamide, apparently formed from hydrolysis of **13** during the purification. Thin-layer chromatography afforded 0.04 g (44% yield) of an oil which was pure **13**, a 57:43 mixture of two diastereomers: IR (film) 1549 ($\nu_{as}(NO_2)$), 1343 ($\nu_s(NO_2)$), 1263 (ν_{as}(N═S═O)), and 1152 (ν_s(N═S═O)) cm^{-1}; ^1H NMR δ 7.5−7.95 (m, 5H), 5.82 (q, 1H maj, J = 6.9 Hz), 5.71 (q, 1H min, J = 7.0 Hz), 3.00 (s, 3H maj), 2.97 (s, 3H min),1.83 (d, 3H min, J = 7 Hz), 1.77 (d, 3H maj, J = 6.9 Hz); ^{13}C NMR δ 134.3, 132.8, 130.3. 130.2, 129.3, 129.2, 97.2, 96.3, 29.6, 29.4, 14.83, 14.78; HRMS (FAB) m/z calcd for $C_9H_{13}N_2O_3S$ [M + H]$^+$, 229.0647, found 229.0651.

Determination of the First pK_a for α-Nitrosulfoximine 2. The general procedure of Bordwell et al.[17] was followed using a Fisher Accumet AB15 pH meter equipped with a standard Accumet 3-in-1 pH/ATC combination electrode (Ag/AgCl internal reference; Fisher catalog no. 13-620-530) to measure pH values. Standard buffer solutions (Fisher Scientific) of pH 7.00 and 4.00 were used for calibration. (Phenylsulfonyl)-nitromethane, nitromethane, and benzoylnitromethane were used as control substances. In all cases, the electrode was immersed in a blank solution of MeOH/H_2O, 50:50, for 2 h or longer prior to a pH measurement. The average pK_a was determined to be 6.30 after a recommended correction factor of −0.10 pH unit was applied for measurements in MeOH/H_2O, 50:50.

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Supporting Information Available: ^1H NMR spectra of **5** and **13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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