sectors. Spectra were calibrated by reference to the oligomeric matrix ions.

UV spectra were recorded on a Uvikon 810P double beam spectrophotometer using 1 cm path length cells. Buffered solutions commonly contained 10^{-5} M antibiotic.

Determination of the sulfur content of the antibiotic was performed at Pfizer Central Research.

Proton NMR spectra were recorded with Brucker WM-250 or AM-400 spectrometers equipped with Aspect 2000 computers. Before analysis, the samples were dissolved in DMSO-d_6, which was then removed in vacuo, and the sample was dried under reduced pressure over phosphorus pentoxide. Spectra were then recorded with these samples dissolved in fresh DMSO-d_6 (99.96 atom %, Aldrich Chemical Co.). Spectral widths of 2500 or 4000 Hz were used (at 250 and 400 MHz, respectively) with quadrature detection employed throughout.

Two-dimensional NMR spectra were acquired in the phase-sensitive mode using quadrature detection in f_2. The spectra consisted of 400-512 increments of t_1. Each t_2 data set was composed of 2K data points, and was the result of 32 transients for the COSY spectra, and 64 transients for the NOESY and CAMELSPIN spectra. The sum of acquisition time and recycle delay was typically 2 s, approximately twice the T_1 value for molecules of this size. NOESY spectra were recorded with a mixing time of 400 ms, and a spin lock field strength of 4 kHz applied for 200 ms was used for the CAMELSPIN experiment. 2-D data sets were multiplied by Lorentzian-Gaussian functions and zero filled to 1K data points in f_1 prior to transformation.

One-dimensional saturation transfer experiments were performed using a recycle delay of 2 s and a preirradiation time of 1.5 s. Sets of 32 transients were acquired with the decoupler alternatively off resonance, and then on resonance with the residual water peak in the DMSO. The resulting FIDs were subtracted and then Fourier transformed.

^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer operating at 100.62 MHz. Waltz-16 was employed for broad-band proton decoupling, with a recycle delay of 2.5 s during which time the decoupler was left on for NOE enhancement. The data was collected over a spectral width of 21 000 Hz and 32K data points. A 2-Hz line broadening was applied prior to transformation.

Type V limpet arylsulfatase enzyme was obtained from Sigma Chemical Co. Typically, 100 mg of antibiotic in 10 mL of 0.2 M sodium acetate buffer, pH 5.0, was incubated with 2 mg (25 units) of enzyme at 36 °C for 48 h. After lyophilization, the mixture was purified by reverse-phase HPLC using a Waters C-18 μ-Bondapak column (9 × 30 mm) and eluted with acetonitrile-0.25 M aqueous ammonium acetate pH 7.8 (1:4) at a flow rate of 3 mL/min.

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Asymmetric Synthesis of Arylglycines

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The asymmetric synthesis of several arylglycines are reported. The methodology deployed involves either cuprate or Friedel-Crafts couplings to chiral bromoglycinates. The % ee's range from 82 to 94%. Both an oxidative and reductive protocol are employed to unmask the oxazinone chiral auxilliary providing the free α-amino acids.

The arylglycines constitute an important class of non-proteinogenic α-amino acids.[1] For example, *p*-hydroxyphenylglycine is a side-chain constituent of the β-lactam antibiotic amoxicillin.[2] Numerous other, highly functionalized arylglycines are found in numerous peptide and glycopeptide antibiotics such as the vancomycins.[3] The apparent simplicity of the arylglycine structure is complicated by the ease of base-catalyzed racemization of the α-methine proton, rendering these substances challenging synthetic targets to obtain in optically pure form.

Numerous approaches to the synthesis of arylglycines have recently appeared, including: enzymatic resolution of racemic Strecker-derived amides and esters;[4] Friedel-Crafts additions to chiral cationic glycine equivalents;[5] asymmetric Strecker reactions;[6] electrophilic amination of chiral enolates;[7] and nucleophilic ring opening of aryl epoxy

Scheme I

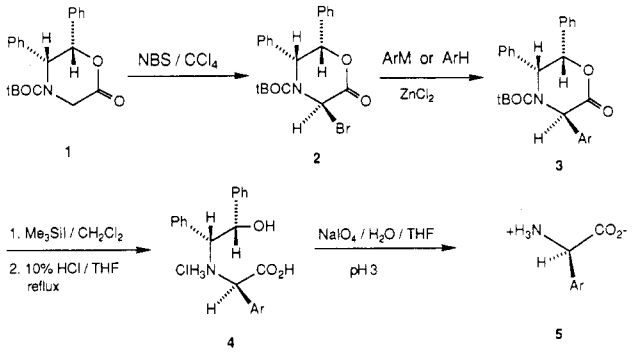

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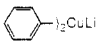
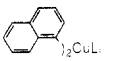
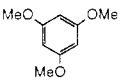
Table I

	ArM/ArH	conditions	% yield (3)	% yield (5)[a]	% ee (5)
a		Et_2O/THF, −78 °C, 1 h	56	52	82
b		Et_2O/THF, −78 °C, 1.5 h	55	29	94
c		$ZnCl_2$/THF, 25 °C, 4.5 h	83[b]	62	91
d		$ZnCl_2$/THF, 25 °C, 5.5 h 4A molecular sieves	50	26	90
e		$ZnCl_2$/MeCN, 25 °C, 4 h 4A molecular sieves	39	73	93

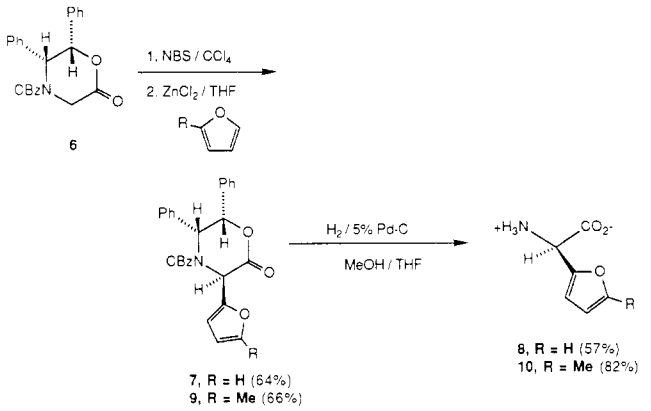
[a] Yield for three steps. [b] Two-step yield for the lactone after TMSI removal of the *t*-BOC group.

alcohols,[8] amongst others.[9] While all of these methods offer avenues to access this increasingly important and difficult functional array, much work in this area remains to be developed to broaden the functional diversity that this class of substances poses. In this paper, we report the further extension of our electrophilic glycinates[10] to the asymmetric synthesis of several arylglycines.

In applying the diphenyloxazinone templates[11] **1** and **6** to the problem of arylglycines, an alternate means of removing the chiral auxilliary needed to be devised that would selectively cleave the C–O and C–N benzylic residues of the auxilliary and not cleave the C–N benzylic bond of the arylglycine unit (**3**, **7**, or **9**) itself. The standard protocol we have developed for effecting destructive removal of the chiral auxilliary involves either a dissolving metal reduction or a catalytic hydrogenation. It was anticipated that neither reaction condition would achieve the desired chemoselectivity. The Strecker-based method of Weinges[6c,d] proceeds through a related 3-aryl-5-phenyl-6-(hydroxymethyl)oxazinone and is reported to be disassembled using either *oxidation* with periodate or reduction on a Raney nickel catalyst. It seemed reasonable that periodate should selectively remove 2 molar equiv of benzaldehyde from the hydroxy acids (**4**), providing the arylglycines in a similar fashion. In the event, we have found that application of the oxidative protocol employed by Weinges provides the desired selectivity on the present substrates.

As illustrated in Scheme I, glycinate **1** is brominated as previously described[10] to furnish the bromide **2**. Reaction of this material with either an arylcuprate or electron-rich

Scheme II



aromatic under Friedel–Crafts conditions provides the anti-arylated substances **3**. Removal of the *t*-BOC group with trimethylsilyl iodide in methylene chloride proceeds cleanly and the lactones are then subjected to hot aqueous HCl to afford the hydroxy acids **4**. Treatment of these crude substances with sodium periodate in (pH 3) aqueous THF, followed by ion-exchange purification, furnishes the free amino acids **5**. The coupling conditions, yields and % ee's are presented in Table I. Varying amounts of partial racemization accompany the final deprotection as diastereochemically homogeneous materials (**3**) are obtained from the couplings to **2**. These seemed to be quite substrate-dependent and consistent for each substance on repeated processing.

We have also found that the *N*-CBz substrate **7** (Scheme II) could be converted into 2-furylglycine (**8**) by a selective three-step method involving: (1) selective removal of the *N*-CBz group with 5% Pd–C/H_2 at atmospheric pressure; (2) ring opening of the lactone (**4**); and (3) periodate cleavage. It is noteworthy that the furan ring is not saturated in the first step, nor oxidized in the last step. In one remarkable instance, we found that the furan adducts **7** and **9** could be cleanly hydrogenated to the corresponding amino acids **8** and **10** in 57% and 82% yield, respectively. This reaction is noteworthy in that, the furan ring is not saturated nor is the "benzylic" C–N moiety of the amino acid cleaved under these conditions. Based on extensive experience hydrogenating these type of oxazinones to the amino acids, we know that the *N*-CBz group is cleaved first followed by the lactone C–O benzylic bond and lastly, the C–N residue. We have been able to isolate these stepwise reduction products by carefully varying the pressure and loading of the catalyst. It would seem reasonable that the anti stereochemistry of **7**/**9** and the relative sluggishness of reducing the furan C–N benzylic residue relative to that of the benzyl C–N bond contribute to the observed se-

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(11) Both antipodes of lactones **1** and **6** are available from Aldrich Chemical Co.; catalogs nos.: (+)-**1**, 33-181-3; (−)-**1**, 33-184-8; (+)-**6**, 33-185-6; (−)-**6**, 33-187-2.

lectivity in these two cases. At higher pressure on a Pd^0 catalyst, substrates **7** and **9** suffer clean conversion to the corresponding 2-tetrahydrofuranylglycine derivatives.[10] We have examined the direct hydrogenation of other α-aryl-*N*-CBz substrates corresponding to **3** but with only limited success. In most cases, small amounts (~10%) of the arylglycine can be obtained under 1 atm of H_2/Pd–C conditions, but myriads of other products are produced. The furan substrates would seem to be an unusual (but reproducible) exception. The oxidative periodate protocol is consistantly successful for all of the aryl substitution we have examined. Further applications of oxazinones **1** and **6** to the synthesis of a variety of complex and sensitive amino acids are under investigation in these laboratories.

Experimental Section

(3*R*,5*R*,6*S*)-4-(*tert*-Butoxycarbonyl)-2,3,5,6-tetrahydro-3,5,6-triphenyl-1,4-oxazin-2-one (3a, Ar = Ph). To a stirred solution of bromobenzene (0.84 mL, 8.00 mmol, 4.00 equiv) in dry Et_2O (4.00 mL) cooled to −15 °C was added *n*-BuLi (4.20 mL, 8.40 mmol, 4.20 equiv, 2.0 M in hexanes) dropwise. The resulting solution was stirred at −15 °C for 30 min when additional dry Et_2O (5.00 mL) was added with copper bromide dimethyl sulfide (0.822 g, 4.00 mmol, 2.00 equiv). The resulting mixture was stirred at −78 °C for 3 h when a solution of the (3*R*,5*R*,6*S*)-3-bromo-4-(*tert*-butoxycarbonyl)-5,6-diphenyl-2,3,5,6-tetrahydro-1,4-oxazin-2-one (**2**) (0.864 g, 2.00 mmol, 1.00 equiv) in a 1:1 solution of dry Et_2O and dry THF (62.00 mL) was added via cannula. Compound **2** was synthesized from compound **1** by standard and previously reported methodology.[10] The resulting mixture was stirred at −78 °C for 1 h when a saturated solution of NH_4Cl (40 mL) was added at −78 °C. The resulting mixture was allowed to warm to room temperature and separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 40 mL). The combined organic layers were washed with 10% HCl (2 × 40 mL), dried ($NaSO_4$), filtered, and evaporated. The residue was separated via column chromatography (7:2:1 Hex/$CHCl_3$/EtOAc) and recrystallized from EtOAc/hexanes, yielding 484 mg (56%) of the desired product (**3a**) as a white solid. ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.59–6.68 (m, 15 H), 6.42 (s) and 6.19 (s) (1 H), 5.85 (d) and 5.76 (d) (1 H), 5.45 (d) and 5.18 (d) (1 H), 1.33–1.13 (m, 9 H). ^1H NMR (200 MHz, DMSO-d_6 at 380 K) δ DMSO: 7.66–7.02 (m, 13 H), 6.72–6.68 (m, 2 H), 6.11 (s, 1 H), 5.95 (d, 1 H), 5.50 (d, 1 H), 1.11 (s, 9 H). IR (NaCl, $CHCl_3$); 3020, 1755, 1695, 1375, 1210, 1150, 1110, 735, 687, 650 cm^{-1}. MS: *m/e* (relative intensity) 428 (0.2), 390 (29.4), 329 (42.6), 284 (76.5), 196 (57.7), 106 (100.0). Mp: 227–228 °C (recrystallization, EtOAc/hexanes). Anal. Calcd for $C_{27}H_{27}NO_4$: C, 75.50; H, 6.34; N, 3.26. Found: C, 75.52; H, 6.61; N, 2.99. $[\alpha]^{25}_D$: +78.2° (*c* 1.00, CH_2Cl_2).

(3*R*,5*R*,6*S*)-2,3,5,6-Tetrahydro-3,5,6-triphenyl-1,4-oxazin-2-one. To a stirred solution of **3a** (250 mg, 0.58 mmol, 1.00 equiv) in dry CH_2Cl_2 (5.80 mL) was added trimethylsilyl iodide (0.20 mL, 1.40 mmol, 2.40 equiv). The resulting orange solution was stirred at room temperature for 10 min, when water (10 mL) was added. The resulting mixture was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layers were washed with 1 M $Na_2S_2O_3$ (2 × 20 mL), dried (Na_2SO_4), filtered, and evaporated. The residue was separated via silica gel column chromatography (5:3:2 Hex/$CHCl_3$/EtOAc) yielding 139 mg (73%) of the desired product as a white foam. ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.63–6.89 (m, 15 H), 5.70 (d, 1 H), 5.21 (s, 1 H), 4.72 (d, 1 H), 2.35 (br s, 1 H). IR (NaCl, $CHCl_3$): 3364, 3029, 2924, 2851, 2359, 1740, 1494, 1453, 1259, 1181, 1065, 757, 694, 689 cm^{-1}. MS: *m/e* (relative intensity) 330 (23.4), 329 (100.0), 327 (71.9), 283 (71.9), 251 (43.7), 196 (51.6), 106 (60.9), 71 (28), 35 (100.0), 31.9 (64.1).

D-Phenylglycine Hydrochloride (5a, Ar = Ph). A stirred solution of (3*R*,5*R*,6*S*)-2,3,5,6-tetrahydro-3,5,6-triphenyl-1,4-oxazin-2-one (93.8 mg, 0.285 mmol, 1.00 equiv) in THF (5.00 mL) and 10% HCl (20.00 mL) was heated at reflux for 15 min. Upon cooling, the solution was evaporated and taken up in distilled water (7.50 mL) and sodium periodate (134 mg, 0.627 mmol, 2.2 equiv), and pH was adjusted to 3.0, and the resulting solution was stirred at room temperature for 36 h. The pH of the resulting suspension was adjusted to approximately 5.5 with the dropwise addition of 0.1 N NaOH, 10 drops of ethylene glycol was added to destroy excess $NaIO_4$, and the mixture was stirred for 15 min. The resulting mixture was washed with EtOAc (3 × 25 mL) and evaporated. The resulting white solid was separated via anion exchange chromatography (Amberlite IRA-45) yielding 38 mg (71%) of D-phenylglycine hydrochloride (**5a**) as a white amorphous solid. Spectral data matches that of authentic material (Sigma).

(3*R*,5*R*,6*S*)-4-(*tert*-Butoxycarbonyl)-5,6-diphenyl-3-(1′-naphthyl)-2,3,5,6-tetrahydro-1,4-oxazin-2-one (3b, Ar = 1-Naphthyl). To a stirred solution of 1-bromonaphthalene (1.68 mL, 12.00 mmol, 4.00 equiv) in dry Et_2O (6.00 mL) cooled to −15 °C was added *n*-BuLi (7.88 mL, 12.60 mmol, 4.20 equiv, 1.60 M in hexanes) dropwise. The resulting white suspension was stirred at −15 °C for 30 min when additional dry Et_2O (7.50 mL) was added with copper bromide dimethyl sulfide (1.233 g, 6.00 mmol, 2.00 equiv). To the resulting thick, dark solution was added dry dimethyl sulfide (3.00 mL) to aid the solubility of the reactants. The resulting mixture was stirred at −78 °C for 3 h when a solution of **2** (1.296 g, 3.00 mmol, 1.00 equiv) in a 1:1 solution of dry Et_2O and dry THF (93.00 mL) was added via cannula. The resulting mixture was stirred at −78 °C for 1.5 h when a saturated solution of NH_4Cl (60 mL) was added at −78 °C. The resulting mixture was allowed to warm to room temperature and separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 60 mL). The combined organic layers were washed with 10% HCl (2 × 60 mL), dried ($NaSO_4$), filtered, and evaporated. The residue was separated via column chromatography (7:2:1 Hex/$CHCl_3$/EtOAc) and recrystallized from EtOAc/Hex, yielding 789 mg (55%) of the desired product as a white solid. ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.24–7.04 (m, 14 H), 6.81 (d, 1 H), 6.64 (dd, 3 H), 5.53 (s, 1 H), 4.85 (d, 1 H), 1.15 (s, 9 H). IR (NaCl, neat): 2970, 1740, 1682, 1381, 1359, 1321, 1268, 1245, 1176, 1150, 1112, 1045, 687 cm^{-1}. MS: *m/e* (relative intensity) 440 (74.2), 380 (58.7), 334 (21.5), 232 (32.9), 215 (100.0), 196 (32.7), 180 (31.1), 156 (22.5), 106 (52.4), 100 (31.4), 58 (34.2). Anal. Calcd for $C_{27}H_{29}NO_4 \cdot 1.5H_2O$: C, 73.50; H, 6.37; N, 2.76. Found: C, 73.64; H, 6.31; N, 2.83. Mp: 214–215 °C (recrystallization, EtOAc/hexanes). $[\alpha]^{25}_D$: +33.9 (*c* 0.99, CH_2Cl_2).

(3*R*,5*R*,6*S*)-5,6-Diphenyl-3-(1′-naphthyl)-2,3,5,6-tetrahydro-1,4-oxazin-2-one. To a stirred solution of **3b** (789 mg, 1.65 mmol, 1.00 equiv) in dry CH_2Cl_2 (16.50 mL) was added trimethylsilyl iodide (0.56 mL, 3.95 mmol, 2.40 equiv). The resulting orange solution was stirred at room temperature for 10 min, when the reaction was quenched with the addition of water (25 mL). The resulting mixture was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 25 mL). The combined organic layers were washed with 1 M $Na_2S_2O_3$ (2 × 40 mL), dried (Na_2SO_4), filtered, and evaporated, yielding a crude yellow oil/foam. The resulting mixture was separated via column chromatography (2:2:1 Hex/$CHCl_3$/EtOAc), yielding 443 mg (71%) of the desired product as a white foam. ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.28–7.16 (m, 10 H), 6.76–6.68 (m, 7 H), 5.83 (d, 1 H), 5.06 (d, 1 H), 4.95 (s, 1 H), 2.50 (br s, 1 H). IR (NaCl, neat): 3322, 2960, 2850, 1725, 1440, 1220, 1182, 1000, 740, 680 cm^{-1}. MS: *m/e* (relative intensity) 287 (0.2), 106 (5.8), 104 (19.1), 88 (83.2), 71 (58.6), 56 (3.6), 35 (100).

D-Naphthylglycine (5b, Ar = 1-Naphthyl). To a stirred solution of (3*R*,5*R*,6*S*)-5,6-diphenyl-3-(1′-naphthyl)-2,3,5,6-tetrahydro-1,4-oxazin-2-one (152 mg, 0.401 mmol, 1.00 equiv) in THF (2.5 mL) was added 10% HCl (5.0 mL). The resulting solution was stirred at room temperature for 1 h and evaporated. The white residue was taken up in water (7.0 mL) and THF (5.0 mL). The pH of the resulting suspension was adjusted to 3 with the dropwise addition of 1 N NaOH. To this solution was added sodium periodate (189 mg, 0.882 mmol, 2.20 equiv), and the resulting mixture was stirred at room temperature for 2 days when the pH was adjusted to 5.5 with the dropwise addition of 1 N NaOH and several drops of propylene glycol were added (to destroy excess $NaIO_4$). The resulting solution was stirred at room temperature for 15 min, the resulting mixture was washed with EtOAc (3 × 5 mL), and the aqueous layer was evaporated, yielding a yellow/white solid mixture which was taken up in water/EtOH and filtered through a C_{18} silica plug and evaporated. This white solid mixture was separated via cation exchange chromatography

(eluted with 1 N NH_4OH, Dowex 50W-X8) yielding 33 mg (41%) of naphthylglycine (**5b**) as a white solid. ^1H NMR (270 MHz, DCl in D_2O) δ HOD: 7.53–7.22 (m, 7 H)8 4.83 (s, 1 H). ^1H NMR (270 MHz, DMSO-d_6) δ DMSO: 8.33 (br s, 1 H), 7.98–7.35 (m, 7 H), 5.01 (s, 1 H), 1.13 (m, 2 H). IR (NaCl, neat): 3380, 3050, 2956, 1594, 1369, 1167, 1047, 1026, 818 cm^{-1}. MS: *m/e* (relative intensity) 171 (20.6), 158 (63.9), 141 (28.8), 128 (3.0), 102 (25.6), 85 (100.0). $[\alpha]^{25}_D$; +8.0° (*c* 0.05, H_2O).[12]

(3*R*,5*R*,6*R*)-5,6-Diphenyl-2,3,5,6-tetrahydro-3-(2′-(1′,3′,5′-trimethoxyphenyl))-1,4-oxazin-2-one (Ar = 1,3,5-Trimethoxyphenyl). To a stirred solution of **2** (0.432 g, 1.00 mmol, 1.00 equiv) in dry THF (7.00 mL) was added 1,3,5-trimethoxybenzene (1.958 g, 11.64 mmol, 11.64 equiv) and zinc chloride (1.33 mL, 2.00 mmol, 2.00 equiv, 1.50 M in THF). The resulting solution was stirred at room temperature for 4.5 h; the solution was then poured into water (10 mL). The resulting mixture was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. Since the residue contained both the *t*-BOC protected and unprotected coupled products it was found to be most efficient to carry the crude mixture on to the *t*-BOC deprotection reaction. Spectral data for the *t*-BOC-protected product (**3c**) is described below. To the yellow solid was added dry CH_2Cl_2 (10.00 mL) and trimethylsilyl iodide (0.28 mL, 2.00 mmol, 2.00 equiv). The resulting deep red solution was stirred at room temperature for 10 min, and water (15 mL) was added. The resulting mixture was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layers were washed with 1 M $Na_2S_2O_3$ (2 × 10 mL), dried (Na_2SO_4), filtered, and evaporated. The oily residue was separated via silica gel column chromatography (6.5:2.5:1.0 Hex/$CHCl_3$/EtOAc), yielding 347 mg (83%) of the desired product as a white foam. ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.21–7.06 (m, 12 H), 5.94 (d, 1 H), 5.41 (s, 1 H) 4.79 (d, 1 H), 3.80 (s, 6 H), 3.78 (s, 3 H), 2.22 (br s, 1 H). IR (NaCl, neat): 3315, 2950, 2850, 1734, 1600, 1488, 1456, 1409, 1330, 1220, 1193, 1140, 1110, 1050, 900, 795, 715, 680 cm^{-1}. MS: *m/e* (relative intensity) 420 (87.5), 375 (2.6), 285 (2.8), 252 (2.9), 210 (25.6), 196 (25.0), 169 (21.1), 104 (22.7), 88 (14.6), 71 (11.2)8 35 (100.0).

(3*R*,5*R*,6*S*)-4-(*tert*-Butoxycarbonyl)-5,6-diphenyl-2,3,5,6-tetrahydro-3-(2′-(1′,3′,5′-trimethoxyphenyl))-1,4-oxazin-2-one (3c). ^1H NMR (270 MHz, $CDCl_3$): δ TMS: 7.26–7.09 (m, 12 H), 6.88 (d, 1 H), 6.51 (d, 1 H), 6.18 (s, 1 H), 3.91 (s, 6 H), 3.83 (s, 3 H), 1.11 (s, 9 H). IR (NaCl, $CHCl_3$): 2968, 2860, 1745, 1695, 1608, 1460, 1448, 1360, 1345, 1225, 1198, 715, 695 cm^{-1}. MS: *m/e* (relative intensity) 520 (0.6), 388 (3.0), 331 (4.0), 306 (3.3), 252 (100.0), 250 (15.0), 196 (14.2), 162 (10.3), 122 (23.3), 106 (26.1), 105 (18.3), 88 (12.4), 58 (12.5), 35 (100.0). Anal. Calcd for $C_{30}H_{33}NO_7$: C, 69.35; H, 6.40; N, 2.70. Found: C, 69.11; H, 6.58; N, 2.48 (obtained as a sticky foam). $[\alpha]^{25}_D$: +61.3° (*c* 0.46, CH_2Cl_2).

D-α-Amino-2,4,6-trimethoxyphenylacetic Acid Hydrochloride (5c, Ar = 1,3,5-Trimethoxyphenyl). A stirred solution of (3*R*,5*R*,6*S*)-5,6-diphenyl-2,3,5,6-tetrahydro-3-(2′-(1′,3′,5′-trimethoxyphenyl))-1,4-oxazin-2-one obtained above (184 mg, 0.440 mmol, 1.00 equiv) in THF (2.90 mL) and 10% $HCl_{(aq)}$ (5.80 mL) was stirred at mild reflux for 30 min. Upon cooling to room temperature, the solution was thouroghly extracted with CH_2Cl_2 (5 × 10 mL), dried (Na_2SO_4), filtered, and evaporated. The resulting residue was taken up in a 1:1 solution of THF and water (9.2 mL) followed by the addition of sodium periodate (207 mg, 0.968 mmol, 2.20 equiv). The pH of the resulting mixture was adjusted to approximately 3 and was stirred at room temperature for 2 days. The pH of the resulting mixture was the adjusted to 7 with the dropwise addition of 1 N NaOH. A white precipitate gradually formed with increasing pH. The resulting neutral solution was allowed to precipitate in the refrigerator overnight. The white solid was collected by filtration, taken up in 10% $HCl_{(aq)}$ and evaporated. The residue was taken up in a minimum amount of 10% $HCl_{(aq)}$, precipitated with the addition of absolute EtOH, filtered, and dried, yielding 66 mg (62%) of the HCl salt of D-α-amino-2,4,6-trimethoxyphenylacetic acid (**5c**) as a yellow solid. ^1H NMR (270 MHz, D_2O) δ HOD: 7.36 (m, 1 H), 7.18 (m, 1 H), 6.11 (s, 1 H), 3.54 (s, 3 H), 3.38 (s, 6 H). IR (NaCl, neat): 3387, 2969, 2848, 1609, 1455, 1417, 1384, 1334, 1208, 1153, 1120, 1054, 949, 817, 700 cm^{-1}. MS: *m/e* (relative intensity) 276 (12.5), 242 (0.3), 210 (17.7), 181 (100.0), 169 (11.2), 106 (20.7), 85 (17.4), 35 (91.8). $[\alpha]^{25}_D$: −14.0° (*c* 0.05, H_2O).[12]

(3*R*,5*R*,6*S*)-4-(*tert*-Butoxycarbonyl)-5,6-diphenyl-3-(2′-furyl)-2,3,5,6-tetrahydro-1,4-oxazin-2-one (3d, Ar = 2-Furyl). To a solution of **2** (0.432 g, 1.00 mmol, 1.00 equiv) in THF (10.00 mL) stirred over powdered molecular sieves (0.5 g, 4 Å) was added furan (1.13 mL, 15.60 mmol, 15.60 equiv) and zinc chloride (2.00 mL, 2.00 mmol, 2.00 equiv, 1.0 M in THF). The resulting solution was stirred at room temperature for 5.5 h when the solution was filtered into water (10 mL). The resulting mixture was extracted with CH_2Cl_2 (4 × 10 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was separated via silica gel column chromatography (7:2:1 Hex/$CHCl_3$/EtOAc), yielding 211 mg (50%) of the desired product as a white solid. ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.47–7.45 (m, 2 H), 7.26–6.97 (m, 6 H), 6.69–6.43 (m, 3 H), 6.31 (s, 1 H), 6.26–6.23 (m, 1 H), 6.09 (s, 1 H), 5.35 (d, 1 H), 5.09 (d, 1 H), 1.36 (s, 4 H), 1.10 (s, 5 H). IR (NaCl, $CHCl_3$): 3130, 2980, 2937, 2874, 1752, 1702, 1501, 1453, 1391, 1350, 1242, 1164, 1055, 952, 883, 757, 716, 701 cm^{-1}. MS: *m/e* (relative intensity) 419 (0.2), 381 (11.3), 320 (9.0), 316 (18.0), 274 (100.0), 244 (3.4), 196 (21.9), 106 (8.8), 96 (6.4), 35 (100.0), 32 (34.4). Anal. Calcd for $C_{25}H_{25}NO_5$: C, 71.58; H, 6.01; N, 3.34. Found: C, 71.79; H, 6.11; N, 3.20. Mp: 202–204 °C (recrystallization, EtOAc/hexanes). $[\alpha]^{25}_D$; −2.4° (*c* 1.00 CH_2Cl_2).

D-α-2-Furylglycine Hydrochloride (5d, Ar = 2-Furyl). To a stirred solution of **3d** (271 mg, 0.646 mmol, 1.00 equiv) in dry $CHCl_2$ (6.50 mL) was added trimethylsilyl iodide (0.22 mL, 1.55 mmol, 2.40 equiv). The resulting red solution was stirred at room temperature for 10 min when the reaction was quenched with the addition of water (6.5 mL). The resulting mixture was separated, the aqueous layer was extracted with CH_2Cl_2 (5 × 10 mL), and the combined organic layers were washed with $Na_2S_2O_3$ (2 × 20 mL) and evaporated. Since the product of this reaction rapidly decomposes, the residue was immediately taken up in THF (4.25 mL), and to this solution was added 10% HCl (8.50 mL). The resulting was stirred at reflux for 15 min, when, upon cooling to room temperature, the pH was adjusted to 3 with the dropwise addition of 1 N NaOH, and sodium periodate (0.304 g, 1.43 mmol, 2.20 equiv) was added. The resulting solution was stirred at room temperature for 2 days, and several drops of ethylene glycol was added to quench the excess sodium periodate. The resulting mixture was stirred at room temperature for 15 min when the mixture was washed with EtOAc (15 mL). The organic layer was washed with water (10 mL), and the pH of the combined aqueous layers was adjusted to 7 with the dropwise addition of 1 N NaOH. The resulting was evaporated to about one-fourth of the original volume and allowed to crystallize in the refrigerator overnight. The resulting mixture was filtered, and the solid material was further purified via anion exchange chromatography (eluted with 10% HCl, Amberlite IR-45), yielding 30 mg (26%) of D-α-2-furylglycine hydrochloride (**5d**) as a white amorphous solid (see data below).

D-α-2-Furylglycine (8). To a stirred suspension of 5% palladium on activated carbon (75 mg) in absolute MeOH (40.00 mL) charged with hydrogen was added a solution of (3*R*,5*R*,6*S*)-4-(benzyloxycarbonyl)-5,6-diphenyl-3-(2′-furyl)-2,3,5,6-tetrahydro-1,4-oxazin-2-one (**7**) (383 mg, 0.846 mmol, 1.00 equiv) in dry THF (11.50 mL) via syringe. Compound **7** was prepared via standard and previously reported conditions.[10] The resulting mixture was stirred at room temperature under hydrogen (1 atm) for 2 h, when the resulting mixture was purged with nitrogen, filtered through Celite, and evaporated to dryness. The predominately white solid was washed with THF and filtered, and the water-soluble white solid was collected and dried. This solid was further purified by filtering an aqueous solution through a C_{18} silica plug followed by cation exchange chromatography (eluted with 1 N NH_4OH, Dowex 50W-X8) and recrystallization from absolute EtOH, yielding 68 mg (57%) of D-furylglycine as a white solid. ^1H NMR

(12) New compounds that were recalcitrant to analytical purification for microanalyses were converted into their corresponding *N*-CBz amino acid derivatives and ester derivatives and compared to known, literature substances. **5b**: Baumgarten, H. E.; Dirks, J. E.; Petersen, J. M.; Zey, R. L. *J. Org. Chem.* **1966**, *31*, 3708 (see also O'Donnel, M. J.; Falmagne, J.-B. *Tetrahedron Lett.* **1985**, *26*, 699). **5c**: Reference 5a. **5d**: Matsumoto, K.; Suzuki, M.; Miyoshi, M. *J. Org. Chem.* **1973**, *38*, 2094. **5e** and **5d**: Ben-Ishai, D.; Sataty, I.; Bernstein, Z. *Tetrahedron* **1976**, *32*, 1571.

(270 MHz, D_2O) δ HOD: 7.43 (d, 1 H), 6.45 (d, 1 H), 6.36 (q, 1 H), 4.84 (s, 1 H). ^1H NMR (DMSO-d_6): δ 7.72 (br, s, 1 H), 6.57 (d, 1 H), 6.49 (br d, 1 H), 5.05 (s, 1 H), 1.87 (m, 2 H). IR (NaCl, mineral oil): 3445, 3169, 3015, 2849, 1605, 1513, 1380, 1215, 1159, 759, 667 cm^{-1}. MS: *m/e* (relative intensity) 142 (17.2), 141 (0.5), 125 (1.5), 111 (3.2), 98 (42.3), 96 (100.0), 93 (30.2), 81 (10.9), 69 (2.9), 64 (3.0), 56 (1.3), 54 (1.6), 46 (1.4), 44 (1.6), 39 (4.9), 35 (100.0), 32 (20.2). Mp: 159–161 °C (recrystallization, absolute EtOH). $[\alpha]^{25}_D$: −32.0° (*c* 0.05, H_2O).[12]

(3*R*,5*R*,6*S*)-4-(*tert*-Butoxycarbonyl)-5,6-diphenyl-3-(2′-(5′-methylfuryl))-2,3,5,6-tetrahydro-1,4-oxazin-2-one (3e, Ar = 5-Methyl-2-furyl). To a solution of **2** (0.432 g, 1.00 mmol, 1.00 equiv) in CH_3CN (7.00 mL) stirred over powdered molecular sieves (1 g, 4-Å) was added 2-methylfuran (1.35 mL, 15.00 mmol, 15.00 equiv), and zinc chloride (2.00 mL, 2.00 mmol, 2.00 equiv, 1.0 M in THF). The resulting solution was stirred at room temperature for 4 h, and the solution was filtered into water (20 mL). The resulting mixture was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The residue was separated via column chromatography (7:2:1 Hex/$CHCl_3$/EtOAc), yielding 170 mg (39%) of the desired product (**3e**) as a white solid. ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.22–6.98 (m, 7 H), 6.69–6.63 (m, 2 H), 6.44 (d, 1 H), 6.38 (d, 1 H), 6.29–6.25 (m, 1 H), 6.05–6.01 (m, 1 H), 5.35 (d, 1 H), 5.11 (d, 1 H), 2.29 (s, 3 H), 1.38 (s, 4 H), 1.09 (s, 5 H). IR (NaCl, $CHCl_3$): 3058, 3021, 2970, 2909, 1758, 1742, 1685, 1591, 1572, 1489, 1445, 1365, 1268, 1211, 1195, 1170, 1160, 1010, 744, 688, 650, 579 cm^{-1}. MS: *m/e* (relative intensity) 434 (0.5), 430 (1.6), 429 (8.8), 428 (29.5), 395 (10.8), 378 (2.5), 334 (7.5), 289 (14.6), 252 (11.4), 214 (29.7), 197 (100), 105 (65.6), 95 (46.1). Anal. Calcd for $C_{26}H_{27}NO_5$: C, 72.04; H, 6.28; N, 3.23. Found: C, 72.02; H, 6.40; N, 3.13. Mp: 213–215 °C (recrystallization, EtOAc/hexanes). $[\alpha]^{25}_D$: −21.2° (*c* 1.00, CH_2Cl_2).

(3*R*,5*R*,6*S*)-5,6-Diphenyl-3-(2′-(5′-methylfuryl))-2,3,5,6-tetrahydro-1,4-oxazin-2-one. To a stirred solution of **3e** (108 mg, 0.249 mmol, 1.00 equiv) in dry CH_2Cl_2 (2.50 mL) was added trimethylsilyl iodide (85 μL, 0.598 mmol, 2.40 equiv). The resulting orange solution was stirred at room temperature for 10 min, and the reaction was quenched with the addition of water (5 mL). The resulting mixture was separated, and the aqueous layer was extracted with CH_2Cl_2 (4 × 5 mL). The combined organic layers were washed with 1 M $Na_2S_2O_3$ (2 × 5 mL), dried (Na_2SO_4), filtered, and evaporated. The resulting oil was separated via PTLC silica gel (7:2:1 Hex/$CHCl_3$/EtOAc) yielding 71 mg (86%) of the desired product as an amber oil. ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.21–6.87 (m, 10 H), 6.30 (d, 1 H), 5.96 (d, 1 H), 5.69 (d, 1 H), 5.24 (s, 1 H), 4.85 (d, 1 H), 2.27 (s, 3 H), 2.15 (br s, 1 H). IR (NaCl, neat): 3330, 3030, 2920, 1750, 1734, 1491, 1448, 1210, 1200, 1195, 1012, 760, 692, 686 cm^{-1}. MS: *m/e* (relative intensity) 334 (2.5), 333 (0.5), 332 (2.6), 288 (2.9), 214 (47.5), 197 (100.0), 105 (51.9), 95 (2.6), 35 (97.3).

D-α-Amino-5-methyl-2-furanacetic Acid (5e, Ar = 5-Methyl-2-furyl). A stirred supension of (3*R*,5*R*,6*S*)-5,6-diphenyl-3-(2′-(5′-methylfuryl))-2,3,5,6-tetrahydro-1,4-oxazin-2-one obtained above (174 mg, 0.521 mmol, 1.00 equiv) in water (4.50 mL) and 10% hydrochloric acid (1.75 mL) was heated at reflux for 30 min. When most of the organic material went into solution, the mixture was cooled to room temperature and washed with CH_2Cl_2 (3 × 3 mL), and the aqueous layer was evaporated. The resulting white solid was taken up in water (10.60 mL), and sodium periodate (0.245 g, 1.15 mmol, 2.20 equiv) was then added. The pH of the resulting suspension was adjusted to 3 with the dropwise addition of 1 N NaOH. The resulting mixture was stirred at room temperature for 36 h when the pH was adjusted to 5.5 with the dropwise addition of 1 N NaOH and several drops of propylene glycol were added (to destroy excess $NaIO_4$). The resulting solution was stirred at room temperature for 15 min and washed with EtOAc (3 × 5 mL), and the aqueous layer was evaporated, yielding a pure white solid mixture. This white solid mixture was separated via cation exchange chromatography (eluted with 1 N NH_4OH, Dowex 50W-X8), yielding 68.6 mg (85%) of D-α-amino-5-methyl-2-furanacetic acid (**5e**) as a white solid. (Spectral data is given below.)

D-α-Amino-5-methyl-2-furanacetic Acid (10). To a stirred suspension of 5% palladium on activated cabon (177 mg) in absolute MeOH (75.00 mL) charged with hydrogen was added a solution of (3*R*,5*R*,6*S*)-4-(benzyloxycarbonyl)-5,6-diphenyl-3-(2′-(5′-methylfuryl))-2,3,5,6-tetrahydro-1,4-oxazin-2-one (**9**) (798 mg, 1.71 mmol, 1.00 equiv) in dry THF (25.00 mL) via syringe. Compound **9** was prepared via standard and previously reported conditions.[10] The resulting mixture was stirred at room temperature under hydrogen (1 atm) for 5 h, and the resulting mixture was purged with nitrogen, filtered through Celite, and evaporated to dryness. The predominately white solid was washed with THF and filtered, and the water-soluble white solid was collected and dried, yielding 216 mg (82%) of D-α-amino-5-methyl-2-furanacetic acid (**10**) as a white solid. ^1H NMR (270 MHz, DMSO-d_6) δ DMSO: 7.87 (br s, 1 H), 6.19 (d, 1 H), 6.01 (d, 1 H), 4.20 (s, 1 H), 3.31 (br s, 2 H), 2.22 (s, 3 H). IR (NaCl, mineral oil): 3413, 3178, 2919, 2849, 2625, 2355, 1608, 1501, 1455, 1378, 1108, 1020, 785, 720 cm^{-1}. MS: *m/e* (relative intensity) 156 (2.3), 155 (0.3), 139 (4.8), 125 (15.7), 110 (52.3), 95 (5.5), 83 (1.1), 52 (7.3), 36 (13.7), 35 (100.0), 32 (20.3). Anal. Calcd for $C_7H_9NO_3$: C, 59.19; H, 5.85; N, 9.03. Found: C, 54.31; H, 6.05; N, 9.18. Mp: 161–163 °C (recrystallization, EtOH). $[\alpha]^{25}_D$: −22.3° (*c* 1.00, H_2O).

General Procedure for CBz Protection of Amino Acids.[12] To a stirred solution of the amino acid (0.100 mmol, 1.00 equiv) in saturated sodium carbonate (0.50 mL) was added benzyl chloroformate (16 μL, 0.110 mmol, 1.10 equiv). The resulting solution was vigorously stirred at room temperature for 30 min to 2 h, and the mixture was thoroughly extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4), filtered, and evaporated. The oily residue could be purified via PTLC or by precipitating with Et_2O followed by recrystallization from CH_2Cl_2.

***N*-(Benzyloxycarbonyl)naphthylglycine.** ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.38–7.25 (m, 12 H), 5.26 (s, 2 H), 5.17 (s, 1 H), 1.56 (s, 1 H). IR (NaCl, $CHCl_3$): 3333, 2956, 2889, 1828, 1761, 1500, 1456, 1372, 1289, 1261, 1150, 1067, 928, 756, 700 cm^{-1}.

***N*-(Benzyloxycarbonyl)furylglycine.** ^1H NMR ($CDCl_3$): δ 11.53 (s, 1 H), 7.32 (s, 5 H), 6.33 (d, 2 H), 5.80 (br s, 1 H), 5.29 (d, 1 H), 5.12 (s, 2 H), 1.22 (s, 1 H). IR (NaCl, $CHCl_3$): 3400, 3067, 3033, 2956, 1744, 1700, 1622, 1494, 1456, 1261, 1217, 1167, 1017, 978, 739, 694 cm^{-1}. MS: *m/e* (relative intensity) 276 (21.6), 275 (16.2), 230 (8.3), 211 (2.4), 198 (25.7), 184 (6.1), 168 (10.8), 141 (1.1), 126 (10.4), 106 (100.0), 88 (30.7), 71 (17.8), 52 (13.3).

***N*-(Benzyloxycarbonyl)-5-methyl-2-furylglycine.** ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 7.34 (s, 5 H), 6.20 (d, 1 H), 5.91 (d, 1 H), 5.45 (d, 1 H), 5.12 (s, 2 H), 2.23 (s, 3 H), 1.25 (br s, 1 H). IR (NaCl, neat): 3333, 2956, 2889, 1750, 1722, 1456, 1344, 1322, 1194, 1067, 967, 928, 733, 700 cm^{-1}. MS: *m/e* (relative intensity) 288 (0.3), 146 (5.7), 104 (0.5), 88 (17.2), 71 (22.8), 58 (14.3), 56 (13.1).

General Procedure for the Esterification of Amino Acids.[12] A stirred suspension of the amino acid (0.050 mmol, 1.00 equiv) in a dry MeOH/HCl solution (0.50 mL) was heated until the amino acid completely dissolved. The resulting solution was cooled to 0 °C, and thionyl chloride (11 μL, 0.155 mmol, 3.10 equiv) was added. The resulting solution was stirred at 0 °C for 1 h and then at room temperature overnight. The resulting solution was evaporated, and the residue was washed with THF. **Naphthylglycine methyl ester.** ^1H NMR (270 MHz, D_2O) δ HOD: 7.98 (m, 3 H), 7.50 (m, 4 H), 5.97 (s, 1 H), 3.68 (s, 3 H). IR (NaCl, $CHCl_3$): 3400, 2922, 2856, 1744, 1722, 1589, 1439, 1133, 1106, 1022, 778 cm^{-1}. MS: *m/e* (relative intensity) 216 (0.8), 215 (0.4), 214 (0.8), 200 (2.5), 171 (4.9), 157 (0.9), 153 (4.0), 141 (1.1), 128 (0.5), 102 (37.4), 88 (1.1), 85 (100.0), 74 (0.4), 71 (5.6), 58 (1.6). **Methyl (α-Amino-2,4,6-trimethoxyphenyl)acetate.** ^1H NMR (270 MHz, $CDCl_3$) δ TMS: 6.07 (m, 2 H), 5.05 (s, 1 H), 3.84 (br s, 9 H), 3.63 (s, 3 H), 1.89 (m, 2 H). IR (NaCl, (NaCl, neat): 3333, 2956, 2922, 2844, 1722, 1611, 1456, 1361, 1344, 1189, 1156, 1122, 1067, 1033, 956, 928, 850, 706 cm^{-1}. MS: *m/e* (relative intensity) 255 (1.9), 241 (1.1), 197 (2.1), 169 (2.3), 119 (2.1), 104 (26.1), 88 (98.4), 71 (100.0), 56 (15.1). **Furylglycine methyl ester.** ^1H NMR (270 MHz, D_2O) δ HOD: 7.50 (d, 1 H), 6.59 (d, 1 H), 6.43 (m, 1 H), 5.39 (s, 1 H), 3.74 (s, 3 H). IR (NaCl, $CHCl_3$): 3411, 2922, 2850, 1743, 1500, 1247, 1154, 926 cm^{-1}.

General Procedure for the Generation of a Mosher (MTPA) Amide.[13] To a stirred suspension of the amino acid

(13) The % ee's determined for each final amino acid was determined by examination of the ^{19}F NMR of the derived MTPA-amides. Authentic racemic amino acids were synthesized and derivatized in like manner to provide the diastereomeric reference signals of the CF_3 groups.

(0.13 mmol, 1.00 equiv) in dry THF (1.00 mL) was added Mosher's chloride (10 μL, 0.13 mmol, 1.00 equiv) and propylene oxide (31 μL, 0.52 mmol, 4.00 equiv). The resulting suspension was heated at reflux for 20 min, when the resulting solution was allowed to cool to room temperature. The solution was filtered and thoroughly evaporated yielding the desired Mosher's amide, usually as a white solid. The % ee's of each amino acid (5) were determined by an examination of the ^{19}F NMR spectra of their respective MTPA amides.

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Chemistry of Tetrathiotungstates: A Novel Synthesis of Disulfides from Sulfonyl Derivatives

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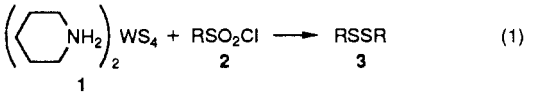
In an unusually novel reaction, piperidinium tetrathiotungstate has been found to induce reductive dimerization of a variety of sulfonyl derivatives to the corresponding disulfides under very mild conditions.

Since sulfonyl chlorides are easily prepared by the chlorosulfonation of arenes and alkanes,[2] their conversion to other organic sulfur compounds with sulfur in the lower oxidation states is synthetically useful. Among these, organic disulfides are important from the point of view of biological activity[3] and industrial utility[4] and are valuable starting materials for the synthesis of a variety of sulfenyl[5] and sulfinyl[6] compounds. Thus the reductive coupling of sulfonyl chlorides to the corresponding disulfides constitutes an important synthetic methodology.

A wide variety of reagents are known to reduce the sulfonyl halides to the corresponding disulfides.[7] Harpp[8] reported an interesting observation where a persulfido complex of molybdenum, $Mo_2S_{12}^{2-}$, induces the formation of *p*-tolyl disulfide from *p*-toluenesulfonyl chloride in acetonitrile at 80 °C in 8 h. Recently, we have shown that alkyl halides can be converted to the corresponding disulfides in excellent yields using piperidinium tetrathiotungstate, 1.[9] While exploring further the synthetic utility of tetrathiotungstate 1 we observed a novel transformation in the reaction of sulfonyl halides to the corresponding disulfides (eq 1). Aryl and alkyl sulfonyl chlorides react



1 2 3 (1)

rapidly with 1 molar equiv of 1 at room temperature to afford the corresponding disulfides in good yield (entries 1-7, Table I). Sulfinyl chloride (entry 8), sulfinic acid (entry 9), α-disulfone (entry 10), and thiosulfonates (entries 11-14) are also smoothly converted to the corresponding disulfides. It is interesting, however, to note that sulfoxide (entry 15), sulfone (entry 16), and sulfonic acid (entry 17), remain unaffected on treatment with 1 even after a long reaction time. In terms of reactivity, alkyl sulfonyl chlo-

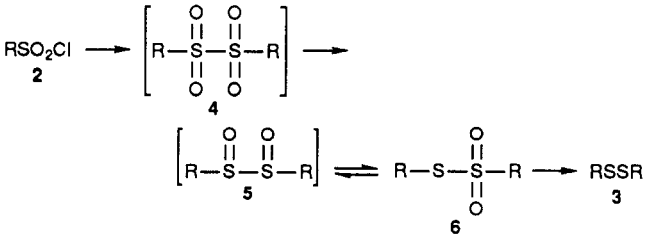
Table I. Reduction of the Sulfonyl Halides and Related Compounds with Piperidinium Tetrathiotungstate

$RSO_2X \xrightarrow{1} RSSR$

entry	substrate	time, h	yield,[a] %
1	$C_6H_5SO_2Cl$, **2a**	2.0	78
2	*p*-CH_3-$C_6H_4SO_2Cl$, **2b**	2.0	69
3	*p*-OCH_3-$C_6H_4SO_2Cl$, **2c**	2.5	61
4	*p*-Br-$C_6H_4SO_2Cl$, **2d**	2.0	53
5	*p*-Cl-$C_6H_4SO_2Cl$, **2e**	2.0	57
6	$C_6H_5CH_2SO_2Cl$, **2f**	4	59
7	$CH_3CH_2CH_2CH_2SO_2Cl$, **2g**	3	41
8	*p*-CH_3-C_6H_4SOCl, **2h**	0.5	96
9	*p*-CH_3-$C_6H_4SO_2H$, **2i**	0.5	98
10	*p*-CH_3-$C_6H_4SO_2SO_2C_6H_4$-CH_3-*p*, **4a**	12	88
11	*p*-CH_3-$C_6H_4SO_2SC_6H_4$-CH_3-*p*, **6a**	0.5	92
12	$C_6H_5SO_2SC_6H_5$, **6b**	0.5	67
13	*p*-CH_3-$C_6H_4SO_2SC_6H_5$, **6c**	0.5	mixture of disulfides
14	*p*-CH_3-$C_6H_4SO_2SC_2H_5$, **6d**	1	mixture of disulfides
15	$C_6H_5SOC_6H_5$, **7**	24	no reaction
16	$C_6H_5SO_2C_6H_5$, **8**	24	no reaction
17	$C_6H_5SO_3H$, **9**	24	no reaction

[a] All compounds gave satisfactory IR, ^1H NMR, mass spectral data, and melting/boiling point.

Scheme I



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