was stirred at 50° for 7 hr while 65 ml of 30% hydrogen peroxide was added in 10-ml portions per hour. The yellow-orange solution was held overnight at room temperature and then concentrated *in vacuo* to a yellow oil. Crystallization from 100 ml of water and 100 ml of ethanol yielded 9.62 g of sulfone. From the mother liquor there was obtained an additional 1.45 g (combined yield 44%). Treatment of an aqueous solution with carbon and recrystallization from 50% ethanol yielded pure *S*-(2-propynyl)-L-cystene *S*-dioxide (1): dec 152°; $[\alpha]^{25}D$ −0.98° (*c* 2.8, H_2O); ir 3270 (HC≡C–), 1605 (ionized carboxyl), and 1135 cm^{-1} (sulfone).

Anal. Calcd for $C_6H_9NO_4S$: C, 37.69; H, 4.74; N, 7.33. Found: C, 37.7; H, 4.67; N, 7.33.

***S*-(2-Propynyl)-L-cysteine *S*-Oxide (2).**—To a solution of 18 g (0.113 mol) of *S*-propargyl-L-cysteine in 1000 ml of acetic acid, there was added 13.0 ml of 32% hydrogen peroxide in 2-ml portions per hour, while the solution was stirred for 8 hr at 25°. The opalescent reaction solution was stirred overnight at room temperature, filtered from a trace of insoluble material, and concentrated *in vacuo* to an oil. Crystallization from 50 ml of water yielded 3.53 g, $[\alpha]^{26}D$ ~0° (water). Crystallization of the mother liquor from ethanol–water with increasing proportions of ethanol yielded the further fractions: 2.77 g, $[\alpha]^{26}D$ −16°; 6.65 g, $[\alpha]D$ −24.7°; 4.27 g, $[\alpha]D$ −41.0° (combined yield 87%). Several recrystallizations of the most levorotatory fraction from aqueous ethanol yielded 450 mg of (−)-*S*-(2-propynyl)-L-cysteine *S*-oxide as prismatic plates: dec 198° (colors 150°); $[\alpha]^{26}D$ −110.1° (*c* 2, water); ir 3190 (s) (HC≡C–), 1630 (s) (ionized carboxyl), and 1005 cm^{-1} (s) (sulfoxide).

Anal. Calcd for $C_6H_9NO_3S$: C, 41.12; H, 5.18; N, 7.99. Found: C, 40.9; H, 5.18; N, 8.03.

Five recrystallizations of the first fraction with $[\alpha]D$ ~0° from water–ethanol (1:4) or aqueous acetone yielded 590 mg of (+)-*S*-(2-propynyl)-L-cysteine *S*-oxide as soft fibrous needles: dec 189°; $[\alpha]^{26}D$ +72.5° (*c* 2, water); ir 3200 (m) (HC≡C–) 1660 (s), 1580 (s) (ionized carboxyl), and 1025 cm^{-1} (s) (sulfoxide).

Anal. Calcd for $C_6H_9NO_3S$: C, 41.12; H, 5.18; N, 7.99. Found: C, 40.7; H, 5.14; N, 7.94.

Cyclization of *S*-(2-Propynyl)-L-cysteine *S*-Dioxide (1).—A solution of 4.86 g (0.0254 mol) of **1** in 1 l. of 2 *N* ammonium hydroxide was kept at room temperature under nitrogen for 2 days. The pale yellow solution was concentrated *in vacuo* to a solid, redissolved in 100 ml of water, and passed through a column of Dowex 50 (H^+) (200 cm^3). The column was eluted with 1300 ml of 2 *N* ammonium hydroxide and the ammonical eluate concentrated *in vacuo* to a solid. Crystallization from 4 ml of water and 30 ml of ethanol yielded 3.39 g of crystalline product. An additional 1.12 g was obtained from the mother liquor (combined yield 85%). Recrystallization from the same solvent system yielded pure 3-(*R*)-carboxy-5-methyl-2,3-dihydro-4*H*-1,4-thiazine *S*-dioxide ammonium salt (**3**) as tiny crystals: dec 185°; $[\alpha]^{26}D$ −0.1° (*c* 4.5, water); ir 3360 (s), 3000–3200 (broad), 1580 (s) (ionized carboxyl), and 1125 cm^{-1} (s) (sulfone).

Anal. Calcd for $C_6H_{12}N_2O_4S$: C, 34.60; H, 5.89; N, 13.45; S, 15.40. Found: C, 34.6 ; H, 5.84; N, 13.2; S, 15.4.

Conversion of the Ammonium Salt (3) to the Hyrochloride.—The ammonium salt (**3**) (4.89 g, 0.0235 mol) was dissolved in 100 ml of cold 3 *N* hydrochloric acid and concentrated *in vacuo* to a solid. Ammonium chloride was removed by crystallization from cold acetone–H_2O (8:1). A yield of 1.12 g (89%) was obtained. The amino acid hydrochloride was obtained from the mother liquor by crystallization from ethanol–acetone (1:15). A yield of 3.86 g of crystalline 3-(*R*)-carboxy-5-methyl-2,3-dihydro-4*H*-1,4-thiazine *S*-dioxide hydrochloride was obtained: dec 173° (sharp); ir 1740 (un-ionized carboxyl) and 1125 cm^{-1} (sulfone).

Anal. Calcd for $C_6H_{10}NO_4SCl$: C, 31.65; H, 4.43; N, 6.15; Cl, 15.57. Found: C, 32.3; H, 4.67; N, 6.17; Cl, 15.3.

Cyclization of *S*-(2-Propynyl)-L-cysteine *S*-Oxide (2) to 4.—A solution of 3.56 g of the sulfoxide ($[\alpha]D$ +1.4°) containing 61% of the (+) isomer and 39% of the (−) isomer in 600 ml of water containing 6 ml of reagent ammonium hydroxide was kept at +3° for 18 hr. The pale amber solution was concentrated *in vacuo* (<20°) to *ca.* 100 ml, decolorized with carbon, and further concentrated *in vacuo* to a solid. Crystallization from 3 ml of water and 18 ml of ethanol yielded 1.50 g of prisms. An additional 0.61 g was obtained from the mother liquor.

The yield of crude product was 88% based on reaction of the (+) isomer. Recrystallization from ethanol–water (5:1) yielded pure 3-(*R*)-carboxy-5-methyl-2,3-dihydro-4*H*-1,4-thiazine *S*-oxide ammonium salt (**4**) as small colorless prisms: dec 182–184° (darkens, 177°); $[\alpha]^{25}D$ +1.0 (*c* 2.4, water); ir 3340 (m), 3000–3100 (broad), 1605 (s) (ionized carboxyl), and 992 cm^{-1} (s) (sulfoxide).

Anal. Calcd for $C_6H_{12}N_2O_3S$: C, 37.49; H, 6.29; N, 14.58; S, 16.68. Found: C, 37.5; H, 6.38; N, 14.6; S, 16.8.

Fractional crystallization from aqueous ethanol or aqueous acetone showed no variation in rotation at the D line and a second sulfoxide could not be obtained. A hydrochloride could not be prepared and addition of acid to the ammonium salt led to decomposition. When cyclization was attempted with pure (−) isomer, only dark resins were obtained.

Registry No.—**1**, 27199-03-7; (+)-**2**, 27199-04-8; (−)-**2**, 27199-05-9; **3**, 27199-06-0; **3** HCl, 27199-07-1; **4**, 27199-08-2.

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field-frequency lock built at this laboratory. Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

A Facile Quantitative Reduction of Sulfoxides

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The recent literature indicates an interest in finding an effective method for the reduction of sulfoxides to sulfides.[1] However, no general method is available which accomplishes the reduction in high yields under mild conditions with common laboratory reagents. A recent report[2] showing the effectiveness of sodium borohydride–transition metal salt systems in the reduction of nitro, amide, and nitrile groups has prompted us to report our findings in sulfoxide reductions.

In connection with our previous work[3] on the novel reduction–dehydration of thioxanthone sulfoxide to thioxanthone and thioxanthenol by sodium borohydride, we found that the same products resulted when the hydroxide ion was replaced by cobalt chloride.[4] However, it was not clear whether the latter reduction again proceeded through a dehydration step or occurred by a simple sulfoxide reduction. Thus, we began an investigation into the effect of this reducing system on sulfoxides.

As shown in Table I, the sodium borohydride–cobalt chloride system reduced dialkyl, arylalkyl, and diaryl sulfoxides, as well as the conformationally restricted[5]

(1) (a) I. Granoth, A. Kalir, and Z. Pelah, *J. Chem. Soc. C*, 2424 (1969), and references cited therein; (b) H. Alper and E. C. H. Keung, *Tetrahedron Lett.*, 53 (1970); (c) K. Naumann, G. Zon, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 2788 (1969); (d) G. V. Kaiser, R. D. G. Cooper, R. E. Koehler, C. F. Murphy, J. A. Webber, I. G. Wright, and E. M. Van Heynengen, *J. Org. Chem.*, **35**, 2430 (1970).

(2) T. Satoh, S. Suzuki, Y. Suzuki, Y. Miyaji, and Z. Imai, *Tetrahedron Lett.*, 4555 (1969).

(3) A. L. Ternay and D. W. Chasar, *J. Org. Chem.*, **32**, 3814 (1967).

(4) D. W. Chasar, Ph.D. Thesis, Case Western Reserve University, Cleveland, Ohio, 1968; *Diss. Abstr.*, **30**, 116B (1969).

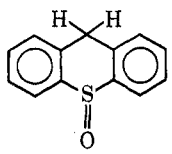
(5) A. L. Ternay, L. Ens, J. Herrmann, and S. Evans, *J. Org. Chem.*, **34**, 940 (1969).

TABLE I

Sulfoxide	Yield of sulfide, %[a]
$(CH_3CH_2CH_2CH_2)_2S(O)$ (5)	98
$C_6H_5S(O)CH_3$ (6)	98
$(C_6H_5)_2S(O)$ (4)	95
Thioxanthene sulfoxide (1)	100
$(C_6H_5CH_2)_2S(O)$ (2)	10
$(CH_2)_4S(O)$ (3)	0

[a] Isolated yields after column chromatography.[6]

thioxanthene sulfoxide **1**, in excellent yields. Thin layer chromatography of the crude products indicated quantitative reduction of the sulfoxide in each of these compounds.[6]



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However, dibenzyl sulfoxide (**2**) and tetramethylene sulfoxide (**3**) afforded little or no sulfide on reduction. In both reductions, the recovery of crude product was low, suggesting possible cleavage reactions[7] leading to volatile products. In the reduction of **2**, some **2** still remained even after extended reaction times, but the major components of the recovered material were two high melting unidentified solids. No sulfide or sulfoxide could be detected (tlc) in the crude product from the reduction of **3**. Both **2** and **3** have also been shown to give poor yields of sulfide by other reduction procedures.[1b,8]

(6) While reduction proceeded quantitatively, an unidentified impurity (<1%) was usually present in the sulfide. This was easily removed by column chromatography.

(7) H. H. Szmant in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, New York, N. Y., 1961, Chapter 16; T. J. Wallace, H. Pobiner, J. E. Hofmann, and A. Schriesheim, *J. Chem. Soc.*, 1271 (1965).

(8) J. Romo, M. Romero, C. Djerassi, and G. Rosenkranz, *J. Amer. Chem. Soc.*, **73**, 1528 (1951).

The investigations of Brown, *et al.*,[9a] and Brown[9b] on the reaction of transition metal ions with sodium borohydride suggest that these reductions may proceed by catalytic hydrogenation. However, it is conceivable that the sulfoxide oxygen coordinates with the metal ion, thus weakening the sulfur–oxygen bond and rendering it more liable to borohydride reduction.[10] Our work toward this end is continuing as well as the applicability of this reducing system to other sulfur-containing functional groups.

Experimental Section

The sulfoxides were either obtained commercially (Aldrich Chemical Co.) or were prepared by oxidation of the corresponding sulfide with *m*-chloroperbenzoic acid according to the procedure of Johnson and McCants.[12] The products were identified by direct comparison of their infrared spectra and tlc behavior with those of authentic sulfides. Thin layer chromatography was performed on precoated glass plates of silica gel using chloroform as eluent and iodine vapor as the visual aid. Column chromatography was accomplished on silica gel (100 mesh) using chloroform as eluent.

Reduction of Diphenyl Sulfoxide (4).—In a typical experiment, sodium borohydride (3.8 g, 0.10 mol) was slowly added to a cooled (10–15°) stirred solution of **4** (2.0 g, 0.01 mol) and cobalt chloride hexahydrate (4.8 g, 0.02 mol) in 200 ml of 95% ethanol. Gas evolved and a black precipitate formed. After complete addition, the mixture was stirred for 2 hr at room temperature. Water (25 ml) was added and the mixture was heated on a steam bath for 5–10 min and then poured into water (300 ml). This mixture was extracted with ether (four 75-ml portions), the extracts were combined and dried ($MgSO_4$), and the solvent was evaporated under vacuum to afford essentially pure sulfide.[6]

Registry No.—**1**, 10133-81-0; **2**, 621-08-9; **3**, 1600-44-8; **4**, 945-51-7; **5**, 2168-93-6; **6**, 1193-82-4.

(9) (a) H. C. Brown, H. I. Schlesinger, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra, and E. K. Hyde, *ibid.*, **75**, 215 (1953); (b) C. A. Brown, *J. Org. Chem.*, **35**, 1900 (1970).

(10) This mechanism would be analogous to that proposed for the reduction of alkoxysulfonium salts by sodium borohydride.[11]

(11) C. R. Johnson, *J. Org. Chem.*, **32**, 3233 (1967).

(12) C. R. Johnson and D. McCants, *J. Amer. Chem. Soc.*, **87**, 1109 (1965).