Calcd for $C_{44}H_{33}ClS$: C, 83.99; H, 5.29. Found: C, 84.22; H, 5.44.

Registry No. **1a**, 67254-57-3; **1b**, 67314-93-6; **2a**, 67254-58-4; **2b**, 67254-59-5; **2c**, 67254-60-8; **3a**, 72478-72-9; **3b**, 72478-73-0; **10a**, 72478-74-1; **10b**, 72478-75-2; **10c**, 72478-76-3; **11a**, 72478-77-4; **11b**, 72478-78-5; **13a**, 72478-79-6; **13b**, 72478-80-9; **15a**, 72478-81-0; **15b**, 72478-82-1; **15c**, 72478-83-2; **16a**, 72478-84-3; **16b**, 72478-85-4; **16c**, 72478-86-5; **17a**, 72478-87-6; **17b**, 72478-88-7; **18a**, 72478-89-8; **18b**, 72478-90-1; **18c**, 72478-91-2; diphenylketene, 525-06-4; fluorenylideneketene *N*-phenylimine, 1749-21-9; tetraphenylallene, 1674-18-6.

Supplementary Material Available: NMR data for **11**, **13**, **15**, **16**, **17**, and **18** (4 pages). Ordering information is given on any current masthead page.

Reductive Coupling of Aromatic Sulfinate Salts to Disulfides[1,2]

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A variety of aromatic sulfinate salts undergo reductive coupling to disulfides in the presence of ethyl hypophosphite. Support for the intermediacy of sulfoxy sulfones and thiosulfonates has been obtained.

We wish to report a new method for the synthesis of disulfides by reductive coupling of sulfinate salts[4] through the agency of ethyl hypophosphite[5,6] (eq 1). Thus, simply

$$\mathrm{ArSO_2M + CH_3CH_2OP(O)H_2 \xrightarrow{Me_2SO} ArSSAr} \qquad (1)$$

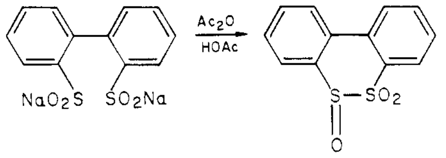
allowing a sulfinate salt to react with ethyl hypophosphite in dimethyl sulfoxide (Me_2SO) overnight gives the corresponding disulfide (see Table I). For example, sodium benzenesulfinate is converted into phenyl disulfide in 64% yield. The reaction seems to be limited to aromatic sulfinate salts since all attempts to reduce aliphatic sulfinates[4] did not yield clean products. Purification by distillation or column chromatography resulted in low recovery of nonpolar material.

Although the mechanism of the conversion of eq 1 is not firmly established, a preliminary investigation has revealed some interesting facts. First, the use of excess ethyl hypophosphite or sulfinate salt lowers the yield of disulfide. For example, a 2:1 ratio of ethyl hypophosphite to sodium benzenesulfinate gives a 52% yield of phenyl disulfide. A 1:2 ratio of these reactants leads to a 36% yield of product. In addition, methyl hypophosphite, available from the ethyl ester by exchange with methanol,[5] also reduces sodium benzenesulfinate to phenyl disulfide in 73% yield. Diethyl phosphite does not react with sodium benzenesulfinate, nor does sodium benzenesulfonate give any organic soluble material when allowed to stir with ethyl hypophosphite in Me_2SO.

These results make sense in view of the recent report by Kice[7a] of intramolecular coupling of sulfinate salts by acetic anhydride (eq 2). Although no mechanism is proposed for this reaction, it is tempting to assume the formation of a mixed anhydride between the sulfinic acid and acetic acid[7b] which then "sulfenylates" the remaining sulfinate salt on sulfur. The analogous reaction in our system is shown in eq 3. Thus, ethyl hypophosphite acts

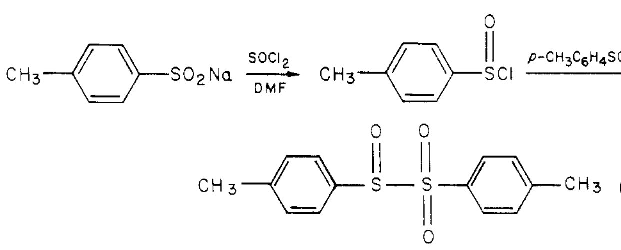
$$\mathrm{C_6H_5SO_2Na \xrightarrow{EtOP(O)H_2} C_6H_5S(O)OP(O)H_2 \xrightarrow{C_6H_5SO_2Na} C_6H_5S(O)S(O)_2C_6H_5 + NaOP(O)H_2} \qquad (3)$$

as an efficient coupling reagent.[8] Diethyl phosphite apparently is unable to function in this way. Sulfonate salts cannot form sulfur–sulfur bonds and therefore do not couple.



(2)

A sulfoxy sulfone was prepared in order to test the feasibility of it as an intermediate (eq 4).[9] This sulfoxy sulfone was allowed to react with ethyl hypophosphite in Me_2SO under the usual conditions to give *p*-tolyl disulfide in 29% yield. Deoxygenation by a phosphorus-containing compound is not surprising since trivalent phosphorus is well-known to convert sulfoxides into sulfides.[10] In ad-



(4)

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(1) A portion of this work was presented at the 30th Southeastern Regional Meeting of the American Chemical Society, Savannah, GA, Nov 8-10, 1978.

(2) Taken in part from the Ph.D. dissertation of Michael A. Reynolds, University of Georgia, 1979.

(3) Undergraduate research participant.

(4) Readily available from organolithium and Grignard reagents plus sulfur dioxide: Pinnick, H. W.; Reynolds, M. A. *J. Org. Chem.* **1979**, *44*, 160.

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(6) To our knowledge the only previous example of disulfide formation from compounds with sulfur in a high oxidation state is the report of the conversion of sulfonyl chlorides into disulfides by trichlorosilane and tri-*n*-propylamine: Chan, T. H.; Montillier, J. P.; Van Horn, W. F.; Harpp, D. N. *J. Am. Chem. Soc.* **1970**, *92*, 7224.

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(8) Acetic anhydride/acetic acid converts sodium benzenesulfinate into the sulfoxy sulfone in poor yield.

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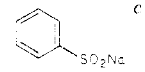
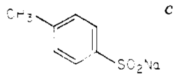
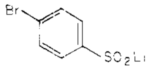
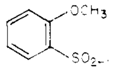
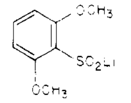
Table I. Preparation of Disulfides

sulfinate salt[a]	% yield of disulfide[b]
 [c]	64
 [c]	31
	48
	50
	51

[a] Prepared as outlined in ref 8 unless otherwise indicated. [b] Nonoptimized yields refer to pure, isolated products. [c] Commercially available.

dition, aryl thiosulfinates are reduced to disulfides by triphenylphosphine.[11] Of course, hypophosphite ion is also present after the coupling of sulfinate salts (eq 3) and represents another trivalent phosphorus species.[12] Indeed, sodium hypophosphite is a very efficient reducing agent for sulfoxy sulfones (eq 5).

$$C_6H_5S(O)S(O)_2C_6H_5 \xrightarrow{NaOP(O)H_2} \underset{100\%}{C_6H_5SSC_6H_5} \qquad (5)$$

Consideration of possible intermediates between the sulfoxy sulfone and the disulfide leads one to conclude that the thiosulfonate is a logical possibility. It is a more likely intermediate than the α-disulfoxide alternative because of the lower reactivity of sulfone sulfur to nucleophilic attack relative to sulfoxide sulfur.[13] Consequently, phenyl benzenethiosulfonate was prepared by oxidation of phenyl disulfide with *m*-chloroperbenzoic acid (MCPBA) (eq 6).[14]

$$C_6H_5SSC_6H_5 \xrightarrow{MCPBA} C_6H_5SS(O)_2C_6H_5 \qquad (6)$$

As expected, this material was reduced to phenyl disulfide by either ethyl hypophosphite (100% yield) or sodium hypophosphite (77% yield) (eq 7).

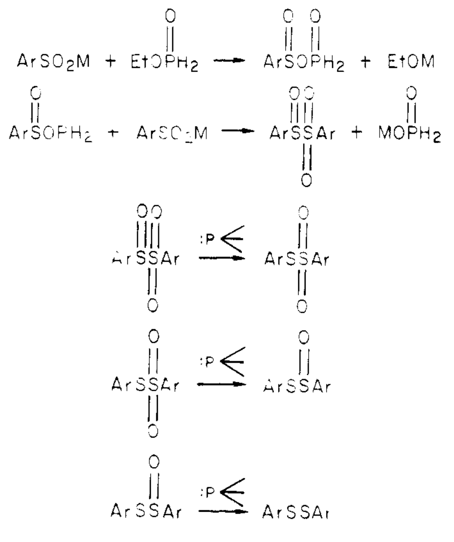
$$C_6H_5SS(O)_2C_6H_5 \xrightarrow{EtOP(O)H_2 \text{ or } NaH_2PO_2} C_6H_5SSC_6H_5 \qquad (7)$$

Stepwise deoxygenation of the thiosulfonate would give initially the thiosulfinate. No attempt was made to test this because of the known[15] rapid disproportionation (eq 8). In any event, the reduction of thiosulfinates to disulfides by phosphines is already established.[11]

$$2C_6H_5SS(O)C_6H_5 \rightarrow C_6H_5SSC_6H_5 + C_6H_5SS(O)_2C_6H_5 \qquad (8)$$

Additional support for this general mechanism for disulfide formation was obtained by monitoring a reaction between ethyl hypophosphite and excess (10 equiv) sodium benzenesulfinate. A spot with an R_f value identical with that of the sulfoxy sulfone was observed upon TLC analysis. Our overall proposed mechanism is given in Scheme I.

Scheme I. Proposed Mechanism for the Conversion of Sulfinate Salts into Disulfides



Experimental Section

Melting points were taken in capillary tubes with a Thomas-Hoover apparatus and are uncorrected. The IR spectra were determined with Perkin-Elmer 237-B, 257, and 297 spectrometers. All NMR spectra were recorded on Varian T-60 and JEOL PFT-100 spectrometers. THF was distilled from potassium. Me_2SO was stored over 4A molecular sieves. Diethyl ether was distilled from calcium hydride and methylene chloride was distilled from phosphorus pentoxide.

Preparation of Lithium 4-Bromobenzenesulfinate. A solution of 11.8 g (50.0 mmol) of *p*-dibromobenzene in 100 mL of dry ether was added to 20.4 mL (50.0 mmol) of 2.45 M *n*-butyllithium/hexane in 10 mL of ether.[16] The reaction mixture was refluxed for 15 min and then added to 50 mL of sulfur dioxide and worked up as usual[4] to give 11.6 g (102%) of white solid: ^1H NMR (D_2O) 7.1 (s).

The salt (1.14 g, 5.00 mmol) was allowed to react with methyl vinyl ketone (0.252 g, 3.60 mmol) and glacial acetic acid (0.300 g, 5.00 mmol) in 15 mL of 95% ethanol as usual[4] to give 4-(4-bromobenzenesulfonyl)butan-2-one (0.62 g, 42%) as pure crystals: mp 123–124 °C; ^1H NMR (acetone-d_6) 2.16 (s, 3 H), 2.90 (t, J = 7 Hz, 2 H), 3.53 (t, J = 7 Hz, 2 H), 7.9 (s, 4 H).

Preparation of Lithium 2-Methoxybenzenesulfinate. A 2.30 M *n*-butyllithium/hexane solution (8.7 mL, 20 mmol) was added to anisole (2.16 g, 20.0 mmol) in 20 mL of dry ether.[17] The reaction mixture was refluxed for 12 h and then added to 10 mL of sulfur dioxide as usual[4] to give 3.10 g (87%) of white solid: ^1H NMR (D_2O) 4.46 (s, 3 H), 7.06 (m, 4 H).

The salt (1.30 g, 7.25 mmol) was allowed to react with methyl vinyl ketone (0.36 g, 5.2 mmol) and glacial acetic acid (0.435 g, 7.25 mmol) in 10 mL of 95% ethanol. The usual workup[4] gave 1.10 g (63%) of pure crystals: mp 90–91 °C; ^1H NMR ($CDCl_3$) 2.23 (s, 3 H), 3.00 (t, J = 8 Hz, 2 H), 3.73 (t, J = 8 Hz, 2 H), 4.08 (s, 3 H), 7.63 (m, 4 H).

Preparation of Lithium 2,6-Dimethoxybenzenesulfinate. A solution of 7.60 g (50.0 mmol) of 1,3-dimethoxybenzene in 30 mL of dry ether was added quickly to 20.4 mL (50.0 mmol) of 2.45 M *n*-butyllithium/hexane.[18] The reaction mixture was stirred for 1 h at room temperature and then added to 60 mL of sulfur dioxide. The usual procedure[4] gave 11.6 g (101%) of white solid: ^1H NMR (D_2O) 3.66 (s, 6 H), 6.86 (m, 3 H).

The salt (1.64 g, 7.90 mmol) was allowed to react with methyl vinyl ketone (0.397 g, 5.70 mmol) and glacial acetic acid (0.474

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(12) The equilibrium between pentavalent and trivalent phosphorus tautomers of hypophosphite ion lies heavily toward the trivalent side: Gallagher, M. J.; Honegger, H. *Tetrahedron Lett.* **1977**, 2987.

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g, 7.90 mmol) in 10 mL of 95% ethanol. The usual workup[4] gave 1.5 g (69%) of viscous oil: bp 120–123 °C (0.05 torr); ^{1}H NMR (CDCl$_3$) 2.23 (s, 3 H), 3.20 (t, J = 7 Hz, 2 H), 3.68 (t, J = 7 Hz, 2 H), 3.93 (s, 6 H), 7.03 (m, 3 H).

Reductive Coupling of Sodium Benzenesulfinate. Ethyl hypophosphite[5] (0.25 g, 2.6 mmol) was dissolved in 50 mL of Me$_2$SO and sodium benzenesulfinate (0.42 g, 2.6 mmol) was added. The reaction mixture was stirred overnight and poured into 50 mL of benzene. The organic layer was washed with three 50-mL portions of water, dried over anhydrous magnesium sulfate, and concentrated. The crude product was filtered through silica gel using 4:1 hexane–benzene to give 0.18 g (64%) of phenyl disulfide:[19] mp 61–62 °C (lit.[20] 61–62 °C).

Reductive Coupling of Sodium *p*-Toluenesulfinate. Ethyl hypophosphite (0.50 g, 5.3 mmol), sodium *p*-toluenesulfinate (0.94 g, 5.3 mmol), and 50 mL of Me$_2$SO gave 0.23 g (31%) of *p*-tolyl disulfide[19] after workup and purification as above: mp 45–46 °C (lit.[21] 47–48 °C).

Reductive Coupling of Lithium 4-Bromobenzenesulfinate. Ethyl hypophosphite (0.47 g, 5.0 mmol), lithium 4-bromobenzenesulfinate (1.1 g, 5.0 mmol), and 50 mL of Me$_2$SO gave 0.45 g (48%) of 4-bromophenyl disulfide[19] after workup and purification as above: mp 88–90 °C (lit.[22] 91–93 °C).

Reductive Coupling of Lithium 2-Methoxybenzenesulfinate. Ethyl hypophosphite (0.47 g, 5.0 mmol), lithium 2-methoxybenzenesulfinate (0.89 g, 5.0 mmol), and 50 mL of Me$_2$SO gave 0.35 g (50%) of 2-methoxyphenyl disulfide[19] after workup and purification as above: mp 116–118 °C (lit.[23] 119–120 °C).

Reductive Coupling of Lithium 2,6-Dimethoxybenzenesulfinate. Ethyl hypophosphite (0.47 g, 5.0 mmol), lithium 2,6-dimethoxybenzenesulfinate (1.0 g, 5.0 mmol), and 50 mL of Me$_2$SO gave 0.42 g (51%) of 2,6-dimethoxyphenyl disulfide[19] after workup and purification as above: bp 145–147 °C.

Reductive Coupling of Sodium Benzenesulfinate with Methyl Hypophosphite. Ethyl hypophosphite (0.94 g, 10 mmol) in 3 mL of methylene chloride was mixed with 3.2 g (100 mmol) of methanol and the mixture was concentrated on a rotary evaporator. The residue was dissolved in 25 mL of Me$_2$SO and 1.6 g (10 mmol) of sodium benzenesulfinate was added. After the solution was stirred overnight and worked up as usual, phenyl disulfide was obtained[19] (0.80 g, 73%), mp 56–57 °C.

Preparation of *p*-Tolyl *p*-Toluenesulfinylsulfonate. Sodium *p*-toluenesulfinate (1.7 g, 9.6 mmol) was added to 0.70 mL (9.6 mmol) of thionyl chloride in 10 mL of petroleum ether containing 6 drops of DMF. After the vigorous reaction ceased, a second portion of sulfinate salt (1.7 g) was added and the reaction mixture was stirred for 24 h at room temperature and then poured into 30 mL of ice water. The solid which formed was collected by filtration, washed with petroleum ether, and dried to give 1.83 g (65%) of the sulfoxy sulfone,[19] mp 85–86 °C (lit.[9a] 87 °C).

Preparation of Phenyl Benzenesulfinylsulfonate. Sodium benzenesulfinate (4.9 g, 30 mmol) was added to 2.1 mL (30 mmol) of thionyl chloride and 6 drops of DMF in 30 mL of petroleum ether. Workup as above gave 5.7 g (71%) of phenyl benzenesulfinylsulfonate,[19] mp 77–78 °C (lit.[24] 78 °C).

Reduction of *p*-Tolyl *p*-Toluenesulfinylsulfonate with Ethyl Hypophosphite. The sulfoxy sulfone (2.9 g, 10 mmol) was stirred overnight with ethyl hypophosphite (1.0 g, 10 mmol) in 50 mL of Me$_2$SO. Workup as usual gave 0.70 g (29%) of *p*-tolyl disulfide,[19] mp 44–45 °C (lit.[21] 47–48 °C).

Reduction of Phenyl Benzenesulfinylsulfonate with Sodium Hypophosphite. The sulfoxy sulfone (2.70 g, 1.01 mmol) was stirred overnight with 0.44 g (5.0 mmol) of dry sodium hypophosphite in 50 mL of ethanol. The reaction mixture was quenched with water and extracted with benzene. After filtration through silica gel, 2.20 g (100%) of phenyl disulfide[19] was obtained; mp 60–61 °C (lit.[20] 61–62 °C).

Preparation of Phenyl Benzenethiosulfonate.[14] Aqueous 30% hydrogen peroxide (10.5 g, 93.6 mmol) was added dropwise over a 30-min period to a suspension of phenyl disulfide (10.0 g, 46.0 mmol) in 37 mL of glacial acetic acid. The reaction mixture was stirred for 24 h at room temperature, cooled to 0 °C, and quenched with 100 mL of water. An oil separated which was dissolved in 30 mL of chloroform. This was washed with aqueous sodium bicarbonate, dried over magnesium sulfate, and concentrated. Filtration through silica gel gave 9.8 g (85%) of phenyl benzenethiosulfonate[19] which was recrystallized from methanol, mp 36–37 °C (lit.[14] 36–37 °C).

Reduction of Phenyl Benzenethiosulfonate with Ethyl Hypophosphite. The thiosulfonate (0.50 g, 2.0 mmol) was stirred overnight with ethyl hypophosphite (0.19 g, 2.0 mmol) in 50 mL of ethanol. The usual workup gave 0.44 g (100%) of phenyl disulfide,[19] mp 61–62 °C (lit.[20] 61–62 °C).

Reduction of Phenyl Benzenethiosulfonate with Sodium Hypophosphite. The thiosulfonate (1.25 g, 5.0 mmol) was stirred overnight with dry sodium hypophosphite (0.44 g, 5.0 mmol) in 25 mL of ethanol. The reaction mixture was quenched with water and extracted with benzene. The organic layers were concentrated and filtered through silica gel to give 0.84 g (77%) of phenyl disulfide,[19] mp 60–61 °C (lit.[20] 61–62 °C).

Registry No. Lithium 4-bromobenzenesulfinate, 72708-54-4; *p*-dibromobenzene, 106-37-6; methyl vinyl ketone, 78-94-4; 4-(4-bromobenzenesulfonyl)butan-2-one, 72708-55-5; lithium 2-methoxybenzenesulfinate, 59057-32-8; anisole, 100-66-3; 4-(2-methoxybenzenesulfonyl)butan-2-one, 72708-56-6; lithium 2,6-dimethoxybenzenesulfinate, 72708-57-7; 1,3-dimethoxybenzene, 151-10-0; 4-(2,6-dimethoxybenzenesulfonyl)butan-2-one, 72708-58-8; sodium benzenesulfinate, 873-55-2; phenyl disulfide, 882-33-7; sodium *p*-toluenesulfinate, 824-79-3; *p*-tolyl disulfide, 103-19-5; 4-bromophenyl disulfide, 5335-84-2; 2-methoxyphenyl disulfide, 13920-94-0; 2,6-dimethoxyphenyl disulfide, 5728-82-5; *p*-tolyl *p*-toluenesulfinylsulfonate, 788-86-3; phenyl benzenesulfinylsulfonate, 784-81-6; phenyl benzenethiosulfonate, 1212-08-4.

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(19) Satisfactory IR and NMR spectra were obtained.

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