uum. The residue, a red, crystalline solid, was collected and washed with anhydrous benzene and dried at 0.1 mmHg (oil pump).

The adducts were characterized by their NMR spectra (Table III) as reported in the Results and Discussion. Small amounts of some other unidentified products are present. This fact and the instability of I and II give a discrepancy in the elemental analysis of the mixture.

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Registry No.---I, 54166-45-9; II, 54166-46-0; 5-nitro-2-methoxythiazole, 26245-61-4; methoxide ion, 3315-60-4.

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Chlorination of Disulfoxides

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Chlorination of (\pm) - and meso-bis(phenylsulfinyl)methane (1a and 1b) with sulfuryl chloride under a variety of conditions gives α -chloro sulfoxides 2a and 2b + 2c, respectively, in high yield with no change in stereochemistry at the sulfur centers. With excess sulfuryl chloride, 1a is dichlorinated to (\pm) -bis(phenylsulfinyl)dichloromethane (3a), which can be reduced, in succession, to α -chloro sulfoxide 2a and then to 1a with either chromous ion or trin-butylphosphine. The role of base (pyridine or sodium bicarbonate) in the chlorination of sulfoxides 1a, 1b, and 2a and phenylsulfinylphenylsulfonylmethane (4) is fundamentally different from the role played by pyridine in the halogenation of bis(phenylsulfonyl)methane.

Recently, α -halo sulfoxides have generated a good deal of interest from both synthesis and mechanism viewpoints.¹ Earlier, we² reported on the syntheses and reductions of α, α -dichloro sulfoxides. We² as well as others⁸ have commented on the problems associated with chlorination of sulfoxides where the intermediate chlorosulfoxium ion is likely to cleave and yield a relatively stable carbenium ion (eq 1). In view of this, a study has been made on the α -chlo-

$$\begin{array}{ccc} O & O \\ PhSCH_2R & \longrightarrow & PhS \\ Cl \end{array} \xrightarrow{\bullet} CH_2R & \longrightarrow & PhSCl + & CH_2R \end{array} (1)$$

rination of sulfoxides bearing the electron-withdrawing (and carbenium ion destabilizing) sulfinyl and sulfonyl groups. Not only should cleavage (eq 1) be precluded in such systems, but with two sulfinyl groups present, the stereochemistry of the reaction at the chiral sulfur could be ascertained, since potentially one diastereomer series could be epimerized over to the other diastereomer series during the chlorination (vide infra).

Results and Discussion

Bis(phenylsulfinyl)methane was synthesized by oxidation of bis(phenylthio)methane with 2 equiv of m-chloroperoxybenzoic acid (MCPBA). The two diastereomers were separated by fractional crystallization and characterized by their known melting points and ¹H NMR spectra.⁴

Several halogenating agents were studied, but N-chlorosuccinimide (NCS), N-bromosuccinimide (NBS), and molecular bromine all proved unreactive toward 1.5 Chlorination with iodobenzene dichloride⁶ produced α -chloro derivatives only in low yields, whereas chlorination with sulfuryl chloride took place readily and in good yields. Therefore, only the reactions of this chlorinating agent were examined in detail.

The reaction of 1a with sulfuryl chloride in dichloromethane in the presence of either pyridine or powdered sodium bicarbonate yielded the single monochloride 2a. Reduction of 2a with either chromous ion² or tri-*n*-butylphosphine² gave only 1a (eq 2). Chlorination of meso-1b gave a



50:50 mixture of 2b and 2c. Reduction of this mixture or reduction of the separated diastereomers with chromous ion or tri-n-butylphosphine gave only 1b (eq 3). If excess

sulfuryl chloride was used, 1a gave the dichloride 3a, which upon reduction $(Cr^{2+} \text{ or } n-Bu_3P)$ gave 2a (eq 4).

$$2a \xrightarrow{SO_2Cl_2 - Py - CH_2Cl_2}_{Cr^{2+} \text{ or } n - Bu_3P} (\pm) - (PhS)_2CCl_2 \qquad (4)$$

All these chlorination reactions proceeded in high yields, and little if any cleavage products were observed. This supports the earlier suggestion^{2,3} that chlorination of sulfoxides will lead to C-S bond cleavage if a stabilized carbenium ion is formed (eq 1). The presence of a second sulfinyl group (R = PhSO) would be clearly a destabilizing factor for the incipient carbenium ion and thus preclude its formation.

Other workers^{6,7} have shown that halogenation α to the sulfinyl group in optically active sulfoxides followed a particular pattern depending upon the specific sulfoxide studied. They observed that during halogenation the sulfur and α -carbon atoms underwent stereospecifically one of the following combinations: inversion-inversion, retention-retention, retention-inversion, or inversion-retention. The particular mode observed depended upon the sulfoxide and the conditions of halogenation; e.g., the presence of silver ion encouraged the double inversion process.^{6b} We observe no change in the stereochemistry at the sulfur centers in 1 resulting from chlorination with sulfuryl chloride or iodobenzene dichloride. Chlorination of 1 with sulfuryl chloride in acetonitrile in the presence or absence of silver nitrate⁶ still led to chlorination with no change in stereochemistry at the sulfur centers.

The chlorination of phenylsulfinylphenylsulfonylmethane (4) with sulfuryl chloride proceeds smoothly in the presence or absence of pyridine. Under the same conditions, molecular bromine gave no reaction. However, treatment of bis(phenylsulfonyl)methane (7) with sulfuryl chloride or bromine in dichloromethane in the absence of base gave no reaction, but in the presence of pyridine, 7 reacted with excess sulfuryl chloride and excess bromine to give the dihalides 8 and 9, respectively.8 The function of pyridine in this latter reaction is to first remove the α proton to generate an α -sulfonyl carbanion, which is subsequently halogenated.9 In the reactions of sulfoxides with sulfuryl chloride, the base (pyridine or bicarbonate ion) either reacts with the intermediate chlorosulfoxium ion and/or simply reacts with the hydrogen chloride generated to prevent acid decomposition of the sulfoxides.¹⁰

$$\begin{array}{c} \bigcap_{PhSCH_2SO_2Ph} & \xrightarrow{SO_2C1_2} & \bigcap_{Py-CH_2C1_2} & \begin{array}{c} O \\ PhSCHCISO_2Ph & \xrightarrow{SO_2C1_2} \\ 4 & & \\ & \\ & &$$

 $(PhSO_2)_2CH_2 \xrightarrow{Py-CH_2CI_2} 8$ (6) $H_{y-CH_2CI_2} (PhSO_2)_2CBr_2$ 9

Experimental Section

Melting points were taken on a Fisher-Johns apparatus and are uncorrected. The ¹H NMR spectra were recorded on a Hitachi Perkin-Elmer R-20 spectrometer at ambient temperature. The spectra were taken in deuteriochloroform with tetramethylsilane (δ 0.00) as an internal standard. Ir spectra were taken in chloroform on a Beckman IR-8 instrument. Elemental analyses were performed by Dr. Franz Kasler of the Department of Chemistry, University of Maryland.

Bis(phenylsulfinyl)methane (1a and 1b). Bis(phenylthio)methane (2.32 g, 0.01 mol) was dissolved in 20 ml of anhydrous ether. To this solution was added 3.46 g (0.02 mol) of 85% MCPBA in 15 ml of anhydrous ether. After 1 hr, 80 ml of dichloromethane was added to dissolve the precipitate, and the solution was washed three times with 10% aqueous sodium carbonate. The organic layer was dried (MgSO₄) and removed by rotary evaporation. A ¹H NMR spectrum of the crude reaction mixture showed it to consist mainly of 1a and 1b (50:50) with a small amount of unreacted starting material and sulfone 5 present. Crystallization from dichloromethane-hexane gave 1a, mp 188-190° (lit.⁴ mp 182-183°), in 40% yield. Repeated fractional crystallizations gave 1b, mp 118-119° (lit.⁴ mp 118-120°), in ca. 10% yield.

Chlorination of 1. To a solution of 1.0 g (3.8 mmol) of 1a dissolved in 18 ml of dry dichloromethane and 2 ml of pyridine was added dropwise 0.55 g (4.1 mmol) of sulfuryl chloride in 3 ml of dichloromethane at room temperature. The course of the reaction could be followed conveniently by TLC (10% ethyl acetate in ether, silica gel) and more sulfuryl chloride added if needed. After 30 min, the solution was washed with 5% hydrochloric acid and dried (MgSO₄) and the solvent was removed by rotary evaporation. A ¹H NMR spectrum of the crude reaction mixture showed the presence of 2a (ca. 90%) and unreacted 1a (ca. 10%). Crystallization from dichloromethane gave 850 mg (75%) of 2a: mp 137–138°; ir $\nu_{S=0}$ 1092 cm⁻¹; ¹H NMR δ 4.93 (s, 1 H) and 7.3–7.9 (m, 10 H).

Anal. Calcd for $C_{13}H_{11}ClO_2S_2$: C, 52.25; H, 3.71. Found: C, 52.42; H, 3.63.

In the same manner, 1b gave a 50:50 mixture of 2b and 2c as shown by ¹H NMR spectroscopy. Fractional crystallization from dichloromethane-pentane gave one diastereomer: mp 148–150°; ir $\nu_{\rm S==0}$ 1085 cm⁻¹; ¹H NMR δ 5.58 (s, 1 H) and 7.3–7.8 (m, 10 H).

Anal. Calcd for $C_{13}H_{11}ClO_2S_2$: C, 52.25; H, 3.71. Found: C, 52.19; H, 3.58.

The second diastereomer isolated exhibited the following physical characteristics: mp 125–126°; ir $\nu_{\rm S=0}$ 1090 cm⁻¹; ¹H NMR δ 5.32 (s, 1 H) and 7.3–7.9 (m, 10 H).

Anal. Calcd for $C_{13}H_{11}ClO_2S_2$: C, 52.25; H, 3.71. Found: C, 52.38; H, 3.78.

When these reactions were run without pyridine but in the presence of anhydrous sodium bicarbonate (heterogeneous reactions), essentially the same results were observed.

In acetonitrile containing 5 ml of pyridine and 1.29 g (7.6 mmol) of silver nitrate, 1a (1.0 g, 3.8 mmol) reacted with 0.785 g (5.7 mmol) of sulfuryl chloride in 2 ml of acetonitrile for 1 hr at room temperature to give ca. a 20% yield of 2a and ca. 0.5 g (50%) of recovered 1a (separated by thick layer chromatography, 10% ethyl acetate-ether, silica gel). The yield of 2a was greatly improved in the absence of silver nitrate.

(±)-Bis(phenylsulfinyl)dichloromethane (3a). To a solution of 0.60 g (2.0 mmol) of 2a dissolved in 10 ml of dichloromethane and 1 ml of pyridine was added dropwise 340 mg (2.5 mmol) of sulfuryl chloride in 2 ml of dichloromethane. The usual work-up and crystallization from dichloromethane-ethanol gave 510 mg (76%) of 3a: mp 174-176° dec; ir $\nu_{S=0}$ 1092 cm^{-1; 1}H NMR δ 7.3-8.2 (m).

Anal. Calcd for $C_{13}H_{10}Cl_2O_2S_2$: C, 46.71; H, 3.02. Found: C, 46.68; H, 2.86.

Reductions of the Chloro Sulfoxides. A. Chromous Ion. To a solution of 0.20 g (0.60 mmol) of dichloro sulfoxide 3a dissolved in 10 ml of acetone and 2 ml of water (deoxygenated by bubbling nitrogen through the solution) was added via syringe 1 ml of ca. 1 M chromous chloride solution (Fischer Scientific). The solution was stirred under nitrogen for 2 hr and then poured into 50 ml of water. This solution was extracted with 2×30 ml of dichloromethane. The organic extracts were combined, dried (MgSO₄), and removed by rotary evaporation. A TLC (20% ethyl acetate in ether on silica gel) showed a trace of 3a and 1a and a major spot which corresponded to monochloro sulfoxide 2a. Crystallization from dichloromethane-hexane gave 130 mg (72%) of 2a, mp 135-137°, undepressed with authentic 2a.

In the same manner, (\pm) -monochloro sulfoxide 2a (0.20 g, 0.67 mmol) in a deoxygenated solution of 8 ml of acetone and 2 ml of water was allowed to react with 2 ml of ca. 1 *M* chromous chloride solution under nitrogen. The reaction was followed by TLC and was essentially complete after 24 hr. The solution was poured into 50 ml of water and extracted with 2 × 30 ml of dichloromethane. The extracts were combined, dried (MgSO₄), and removed by rotary evaporation. Crystallization from dichloromethane-hexane gave

170 mg (96%) of (±)-disulfoxide 1a, mp 185-189°, undepressed with authentic la.

Treatment of 0.65 mg of a 2:1 mixture of meso: (\pm) -disulfoxides (1b and 1a, respectively) under the above reaction conditions gave no discernible change in the distribution of diastereomers.

B. Tri-n-butylphosphine. A solution of 0.20 g (0.60 mmol) of dichloro sulfoxide 3a and 0.13 g (0.60 mmol) of tri-n-butylphosphine in 8 ml of methanol (under nitrogen) stood at room temperature for 30 min. Work-up (water-dichloromethane extraction) gave 0.125 (68%) of 2a, mp 134-136°.

A solution of 0.20 g (0.67 mmol) of 2a and 140 mg (0.67 mmol) of tri-n-butylphosphine in 5 ml of methanol (under nitrogen) stood at room temperature for 2 hr. The crystals that formed were filtered and washed with cold ether (3 ml) to give 115 mg of (\pm) -1a, mp 191-193°. The mother liquor yielded an addition 0.04 g of 1a, total yield 0.165 g (90%).

Treatment of meso disulfoxide 1b with dilute HCl in methanol in the presence or absence of tri-n-butylphosphine or tri-n-butylphosphine oxide gave no sign of epimerization to diastereomer 1a.

Chlorination of Phenylsulfinylphenylsulfonylmethane (4). To a solution of 0.50 g (1.8 mmol) of 4^{11} and 0.50 g of sodium bicarbonate in 12 ml of dichloromethane was added dropwise 0.26 g (1.9 mmol) of sulfuryl chloride in 2 ml of dichloromethane. The reaction mixture was treated as in the analogous case of the chlorination of (\pm) -la. An NMR spectrum of the crude reaction mixture showed a trace of unreacted 4 and two singlets (4:1 ratio) at δ 5.2 and 5.4, respectively. Crystallization from dichloromethane-hexane gave 310 mg (58%) of the major isomer (5a): mp 115-116°; ir $\nu_{\rm SO_2}$ 1333 and 1142, $\nu_{\rm S=0}$ 1095 cm⁻¹; ¹H NMR δ 5.25 (s, 1 H) and 7.3-8 (m, 10 H).

Anal. Calcd for C13H11ClO3S2: C, 49.59; H, 3.52. Found: C, 49.57; H. 3.47.

Further crystallization yielded 50 mg (9%) of the other diastereomer 5b: mp 124–126°; ir ν_{SO_2} 1340 and 1135, $\nu_{S=0}$ 1092 cm⁻¹; ¹H NMR δ 5.43 (s, 1 H) and 7.3-8 (m, 10 H).

Anal. Calcd for C13H11ClO3S2: C, 49.59; H, 3.52. Found: C, 49.44; H. 3.60.

A similar result to the above was obtained when chlorination was run in the presence of pyridine instead of sodium bicarbonate. Phenylsulfinylphenylsulfonyldichloromethane (6). To a so-

lution of 0.300 g (1.07 mmol) of 4 in 12 ml of dichloromethane and 1 ml of pyridine was added 0.40 g of sulfuryl chloride in 2 ml of dichloromethane at room temperature. The solution stood for 1 hr and was worked up as usual. Crystallization from dichloromethane-hexane gave 0.315 g (90%) of 6: mp 135-136° (from dichloromethane-ethanol); ir ν_{SO_2} 1152 and 1350, $\nu_{S=0}$ 1100 cm⁻¹; ¹H NMR δ 7.3-8.2 (m).

Anal. Calcd for C13H10Cl2O3S2: C, 44.58; H, 2.88. Found: C, 44.49: H. 2.82.

Halogenation of Bis(Phenylsulfonyl)methane (7). To a solu-

tion of 0.90 g (3.0 mmol) of 7 in 10 ml of dichloromethane and 3 ml of pyridine was added 0.80 g of sulfuryl chloride in 2 ml of dichloromethane. After 1 hr, the mixture was diluted with 50 ml of dichloromethane, washed with 5% sodium bicarbonate (100 ml), and dried (MgSO₄) and the solvent was removed by rotary evaporation. Crystallization of the resulting oil gave 1.0 g (85%) of bis-(phenylsulfonyl)dichloromethane (8), mp 157-159° (lit.¹² mp 159°).

In a similar manner, 7 treated with excess bromine gave an 80% yield of bis(phenylsulfonyl)dibromomethane (9), mp 156-158° (lit.¹² mp 159°). This dibromide was converted back to 7 quantitatively by sodium thiosulfate in aqueous acetone.

Registry No.-1a, 27995-61-5; 1b, 27995-60-4; 2a, 54384-32-6; 2b, 54423-03-9; 2c, 54423-04-0; 3a, 54384-33-7; 4, 54384-18-8; 5a, 54384-34-8; 5b, 54384-35-9; 6, 54384-19-9; 7, 3406-02-8; sulfuryl chloride, 7791-25-5; bis(phenylthio)methane, 3561-67-9.

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Substituent Effects on the Efficiency of Hydrogen Migration vs. **Electrocyclic Ring Closure in 1,2-Benzotropilidenes**

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The photochemistry of 5-carbomethoxy- (1b), 5-cyano- (1g), 5-methyl- (1e), and 5-vinyl- (1f) 1,2-benzotropilidenes has been studied. Two major processes arise from the singlet excited state of these molecules: (1) production of benzonorcaradienes via a formal 1,7-hydrogen shift followed by tautomerization, and (2) electrocyclic ring closure to produce 6-substituted 2,3-benzobicyclo[3.2.0]hepta-2,6-dienes. While the overall quantum efficiency for the compounds is high ($\Phi = 0.53-0.85$), the relative importance of the two processes is markedly substituent and modestly solvent dependent. The 5-cyano- and 5-carbomethoxy-1,2-benzotropilidenes give major amounts of electrocyclic ring closure while the remaining compounds give primarily hydrogen migration. The increased efficiency of the hydrogen shift process in going from cyclohexane to acetonitrile suggests a polar character in the transition state for this reaction.

The photochemistry of cycloheptatrienes has been subject to extensive study over the past 10 years.² While electrocyclic ring closure of cycloheptatrienes to bicyclo-

[3.2.0]hepta-2,6-dienes was apparently noted first,^{2a} later work established that photochemical 1,7-hydrogen shift occurs some 500 times faster than cyclobutene formation.^{2e}