Cycloaddition of 1 to Methyl Crotonate. Method B (200 °C; 24 h) yielded 42% (80% relative to unreacted starting material as determined by NMR of the crude reaction mixture) of a clear liquid, 1,2-bis(trimethylsilyloxy)-4-carbomethoxy-5-methyl-1-cyclohexene, after Kugelrohr distillation at 105 °C (0.002 mm). The adduct gave the following spectral data: IR (neat) 3.4, 5.75, and 5.86 μm; NMR (CCl_4) δ 0.12 (s, 9 H), 0.14 (s, 9 H), 0.92–1.03 (m, 3 H), 1.67–2.50 (m, 6 H), and 3.68 (s, 3 H); mass spectrum *m/e* (rel intensity) 330 (100), 230 (18), 182 (20), 165 (16), 147 (48), 73 (99), 58 (14), 43 (48), and 28 (17). Anal. Calcd for $C_{15}H_{30}O_4Si_2$: C, 54.50; H, 9.14. Found: C, 54.25; H, 9.13.

Cycloaddition of 1 to Benzoquinone. Method A (24 h) using 3 equiv of benzoquinone to minimize 2:1 cycloadduct formation yielded 78% of a yellow solid 6,7-bis(trimethylsilyloxy)-5,8,9,10-tetrahydro-1,4-naphthoquinone (mp 81.5–83 °C) which gave the following spectral absorptions: IR (KBr) 3.4 and 6.0 μm; NMR (CCl_4) δ 0.13 (s, 18 H), 2.0–2.75 (m, 4 H), 3.05–3.35 (m, 2 H), and 6.63 (s, 2 H); mass spectrum *m/e* (rel intensity) 338 (50), 147 (23), 73 (100), and 45 (13). Anal. Calcd for $C_{16}H_{26}O_4Si_2$: C, 56.77; H, 7.74. Found: C, 56.54; H, 7.81.

Cycloaddition of 1 to Maleic Anhydride. Method A (24 h) yielded 61% of a white solid, 4,5-bis(trimethylsilyloxy)-1,2,3,6-tetrahydrophthalic anhydride (mp 51–51.5 °C), with the following spectral absorptions: IR (KBr) 3.4, 5.4, and 5.75 μm; NMR ($CDCl_3$) δ 0.16 (s, 18 H), 2.57–2.67 (m, 4 H), and 3.33–3.47 (m, 2 H); mass spectrum *m/e* (rel intensity) 328 (31), 167 (18), 147 (43), 75 (24), 73 (100), and 45 (13). Anal. Calcd for $C_{14}H_{24}O_5Si_2$: C, 51.19; H, 7.36. Found: C, 50.96; H, 7.40.

Oxidation of Cycloadduct 2. The cycloadduct **2** (65.8 g, 0.177 mol) and sulfur (5.66 g, 0.177 equiv) were heated with stirring in a 250-mL round-bottom flask fitted with a condenser. At 210 °C the mixture vigorously evolved hydrogen sulfide gas. The vessel was maintained at 210 °C for 15 min and then cooled. The reaction mixture was diluted with 100 mL of carbon tetrachloride and 35 g of copper power (previously washed with dilute hydrochloric acid, water, acetone, and finally carbon tetrachloride) was added to remove any unreacted sulfur. The solid materials were filtered off, the solvent was rotary evaporated, and the product was distilled under vacuum (0.002 mm, 120–125 °C) to yield 62.44 g (95.3%) of a clear liquid, dimethyl 4,5-bis(trimethylsilyloxy)phthalate (**3**). The phthalate derivative showed the following spectral absorptions: IR (neat) 3.4 and 5.8 μm; NMR (CCl_4) δ 0.27 (s, 18 H), 3.83, (s, 6 H), and 7.17 (s, 2 H); mass spectrum *m/e* (rel intensity) 370 (92), 339 (17), 251 (100), and 73 (92). Anal. Calcd for $C_{16}H_{26}O_6Si_2$: C, 51.86, H, 7.07. Found: C, 51.77; H, 7.08.

Hydrolysis of 3. The phthalate **3** (61.8 g, 0.167 mol) was stirred with 100 mL of water at room temperature overnight. The water and hexamethyldisiloxane were rotary evaporated to yield 37.6 g (99.6%) of a white solid, dimethyl 4,5-dihydroxyphthalate. Recrystallization from Skellysolve B/ethyl acetate gave white needles, mp 141.5–142.5 °C, with the following spectral properties: IR (KBr) 2.9, 3.0, 3.4, 5.8, 5.9, and 6.2 μm; NMR (acetone-d_6) δ 3.80 (s, 6 H), 7.25 (s, 2 H), and 8.83 (br s, 2 H); mass spectrum *m/e* (rel intensity) 226 (42), and 195 (100). Anal. Calcd for $C_{10}H_{10}O_6$: C, 53.10; H, 4.46. Found: C, 53.14; H, 4.49.

Conversion of Dimethyl 4,5-Dihydroxyphthalate to Imide 5. Dimethyl 4,5-dihydroxyphthalate (33.47 g, 0.148 mol) was dissolved in 500 mL of dry acetone. Potassium carbonate (90 g, 0.652 mol) and dimethyl sulfate (41 g, 0.326 mol) were added and the solution was refluxed with stirring under a nitrogen atmosphere for 8 h, at which point the solution gave a negative ferric chloride test. The salts were filtered off and the acetone was removed by rotary evaporation. Water (50 mL) was added and the organic product was extracted with three 300-mL portions of ether. The ether layers were combined, washed with water, and dried over magnesium sulfate and the ether was rotary evaporated to yield 35.4 g (94%) of a white solid, dimethyl 4,5-dimethoxyphthalate, mp 88–89 °C, with the following spectral properties: IR (KBr) 3.33, 3.4, 5.78, 5.84, and 6.27 μm; NMR (CCl_4) δ 3.80 (s, 6 H), 3.87 (s, 6 H), and 7.04 (s, 2 H); mass spectrum *m/e* (rel intensity) 254 (66) and 223 (100).

The dimethoxyphthalate (34.35 g, 0.135 mol) was saponified by refluxing in 125 mL of 10% aqueous sodium hydroxide solution for 3 h. The solution was cooled and acidified to pH 1 with concentrated hydrochloric acid and the precipitate was filtered off and dried under vacuum to yield 26.9 g (88%) of a white solid, 4,5-dimethoxyphthalic acid, mp 198–199.5 °C dec (lit.[9] mp 193–199 °C). The phthalic acid derivative (**4**) gave the following spectral absorptions: IR (KBr) 3.1–3.6 (br), 4.2 (br), 5.85, 6.12, and 6.3 μm; NMR (Me_2SO-d_6) δ 3.83 (s, 6 H) and 7.23 (s, 2 H); mass spectrum *m/e* (rel intensity) 226 (100).

The diacid **4** (26.5 g, 0.117 mol), urea (14 g, 0.234 mol), and 250 mL of ethylene glycol were heated with stirring to 180 °C until no more ammonia evolved as tested by pH paper. The solution was cooled and the product was filtered off, washed with water, and dried under vacuum to yield 23.1 g (95%) of a cream-colored solid, 4,5-dimethoxyphthalimide. Recrystallization from acetic acid gave white needles, mp > 320 °C (lit.[10] mp >300 °C), with the following spectral properties: IR (KBr) 3.02, 5.7, 5.8, and 6.25 μm: NMR (Me_2SO-d_6) δ 3.88 (s, 6 H) and 7.33 (s, 2 H); mass spectrum *m/e* (rel intensity) 207 (12), 206 (100), 192 (19), 164 (12), 136 (20), and 121 (22).

Registry No.—**1**, 31411-71-9; **3**, 66323-02-2; **4**, 577-68-4; **5**, 4764-20-9; 1,2-bis(trimethylsilyloxy)cyclobutene, 17082-61-0; hydroquinone, 123-31-9; dimethyl 4,5-dihydroxyphtholate, 66323-03-3; dimethyl 4,5-dimethoxyphthalate, 17078-61-4; urea, 57-13-6.

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Peroxy Acid Oxidation of Alkyl Phenyl Disulfides

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The oxidation of an unsymmetrical disulfide, RS–SR′, with 2 equiv of a suitable oxidizing agent might yield two possible thiolsulfonates, namely, RSO_2–SR′ and RS–SO_2R′, provided no cleavage of the S–S bond occurs in the course of the oxidation. Depending on the nature of the substituent groups, one might expect to observe a preponderance of one isomeric product over the other.[1] In connection with another study, we found it desirable to establish the relative reactivity of phenyl- vs. alkyl-substituted sulfur atoms toward peroxy acid in such unsymmetrical disulfides. Toward this end, the peroxy acid oxidation of ethyl phenyl disulfide (**1**) and benzyl disulfide (**2**) was studied.

$$\underset{\mathbf{1}}{CH_3CH_2SSC_6H_5} \xrightarrow{\text{MCPBA}} \underset{\mathbf{1a}}{CH_3CH_2SO_2SC_6H_5}$$

$$\underset{\mathbf{2}}{C_6H_5CH_2SSC_6H_5} \xrightarrow{\text{MCPBA}} \underset{\mathbf{2a}}{C_6H_5CH_2SO_2SC_6H_5}$$

Upon oxidation of ethyl phenyl disulfide (**1**) with 2.3 equiv of *m*-chloroperoxybenzoic acid (MCPBA), phenyl ethanethiolsulfonate (**1a**) was formed as the major product in ca. 75 ± 10% yield. Similarly, oxidation of **2** with MCPBA (2.0 equiv) afforded **2a** in ca. 65% yield. In both reactions, considerable amounts of difficultly separable materials were produced; however, none of the possible alternate isomeric products, ethyl benzenethiolsulfonate (**1b**) or benzyl benzenethiolsulfonate (**2b**), respectively, were detectable in the crude oxi-

$$\underset{\mathbf{1b}}{CH_3CH_2SSO_2C_6H_5} \qquad \underset{\mathbf{2b}}{C_6H_5CH_2SSO_2C_6H_5}$$

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dation products as determined by ^1H NMR spectral assays using, for comparison, ^1H NMR spectral characteristics of authentic **1b** and **2b** which had been independently prepared (the latter also is an intermediate in the preparation of **2**; see Experimental Section).

The selectivity observed in the above oxidations becomes explicable if one views the sulfur bound to phenyl in **1** and **2** as being the relatively electron-poor sulfur center in each disulfide, due to delocalization of its electrons into the phenyl ring and/or to a relatively greater electron-donating ability of the ethyl group in **1**, or benzyl group in **2**, to the remaining sulfur atom. Thus, initial reaction of disulfide **1** or **2** with an electrophilic reagent such as MCPBA would be expected to occur at the latter more electron-rich (nucleophilic) sulfur to produce the corresponding thiolsulfinate[2] which, upon further reaction with peroxy acid, presumably undergoes preferential oxidation at the already partially oxidized sulfur atom[3,4] to yield the observed thiolsulfonate.

We have observed that less than 35% of the total final product is unaccounted for in each of the two oxidations studied and that this lesser portion of the total product in each case includes no detectable amounts of **1b** or **2b** (as already mentioned above), or of either of the two predicted products of "scrambling" of the S–S linked portions of **1** or of **2** due to disproportionation via an α-disulfoxide[4] derivable from any intermediate thiolsulfinate(s) formed. Hence, it seems reasonable that the straightforward course of oxidation suggested above for **1** and **2** is the major pathway operative in the peroxy acid oxidation of *alkyl aryl disulfides* and that electronic effects are of primary importance in determining the regiospecificity of the initial oxidation of such disulfides to thiolsulfinates.[5] In this respect our results also accentuate similar conclusions already put forth by Block and O'Connor[2] concerning the importance of electronic effects on the outcome of the peroxy acid oxidations of unsymmetrical dialkyl disulfides to thiolsulfinates.

Experimental Section

Preparation of Ethyl Phenyl Disulfide (1).[6] A solution of 0.16 g (0.002 mol) of pyridine in 7 mL of absolute ethanol was added dropwise during 15 min to a stirred solution of 0.53 g (0.002 mol) of phenyl α-toluenethiolsulfonate (**2a**)[7] and 0.13 g (0.002 mol) of ethanethiol in 20 mL of absolute ethanol at 0–3 °C. The reaction mixture was stirred at 0–3 °C for 15 min and at 20 °C for 5.5 h. The solution was diluted with water and extracted with diethyl ether. The combined organic extracts were washed with dilute $NaHCO_3$ solution and water and dried ($MgSO_4$). The solvent was evaporated in vacuo below 30 °C to yield 0.30 g (88%) of an oily residue which on evaporative distillation afforded 0.20 g (58%) of pure **1** as a pale yellow oil: bp 46 °C (0.1 mm) [lit. bp 126 °C (15 mm),[6a] 89–90 °C (1.2 mm),[6b] 66 °C (0.1 mm)[6c]; ^1H NMR ($CDCl_3$) δ 1.30 (t, J = 7 Hz, 3), 2.75 (q, J = 7 Hz, 2), and 7.0–7.7 (m, 5).

Formation of Phenyl Ethanethiolsulfonate (1a) by Oxidation of Ethyl Phenyl Disulfide (1) with *m*-Chloroperoxybenzoic Acid (MCPBA). A solution of 475 mg (ca. 2.3 mmol) of MCPBA (85% pure; Aldrich Chemical Co.) in 10 mL of CH_2Cl_2 was added during 45 min to a stirred solution of 180 mg (ca. 1.0 mmol) of **1** in 10 mL of CH_2Cl_2 at −24 °C. Stirring was continued for 2 h below −20 °C followed by an additional 16 h at +20 °C. A ^1H NMR spectrum of a $CDCl_3$ solution of the total crude product in an aliquot removed from the reaction mixture at this point revealed that, in addition to a small amount of dissolved *m*-chlorobenzoic acid, **1a** was the only major product present (ca. 75 ± 10% by ^1H NMR assay); *no detectable amount* (i.e., <3%) *of* **1b** *was evident*. The reaction mixture, after partial concentration in vacuo and removal of the insoluble *m*-chlorobenzoic acid, was evaporated to dryness. The residue was fractionally crystallized several times from CCl_4, yielding 185 mg (84%) of crude **1a** which was ca. 80% pure by ^1H NMR assay. Recrystallization from diethyl ether gave 80 mg (37%) of **1a** as colorless crystals: mp 50–52 °C (lit.[8] mp 52 °C); ^1H NMR ($CDCl_3$) δ 1.4 (t, J = 7 Hz, 3), 3.2 (q, J = Hz, 2), and 7.2–7.8 (m, 5).

Preparation of Ethyl Benzenethiolsulfonate (1b). The following procedure was adapted from a procedure described by Boldyrev et al.[8] A solution of 0.62 g (0.010 mol) of C_2H_5SH in 30 mL of CCl_4 was added dropwise to a stirred solution of 2.1 g (0.013 mol) of Br_2 in 50 mL of CCl_4 during 10 min at −25 to −20 °C. Nitrogen was bubbled through the solution for 0.5 h (to remove HBr). Benzene (50 mL) and a mixture of 2.0 g of benzenesulfinic acid (excess) in 50 mL of water were added to the above solution, and stirring was continued for an additional 10 min. The aqueous layer was discarded. The benzene layer was washed with dilute $NaHCO_3$ solution and extracted with CH_2Cl_2. The combined organic extracts were washed with water and dried ($MgSO_4$). Evaporation of the solvent in vacuo afforded 2.5 g of a pale yellow oil which on vacuum distillation gave 1.80 g (89%) of pure **1b** as a colorless oil: bp 104–106 °C (0.15 mm) [lit.[8] bp 90–91 °C (0.10 mm)]; ^1H NMR ($CDCl_3$) δ 1.26 (t, J = 7.5 Hz, 3), 3.03 (q, J = 7.5 Hz, 2), 7.4–7.8 (m, 3), and 7.8–8.1 (m, 2).

Preparation of Benzyl Phenyl Disulfide (2).[9,10] A solution of 0.40 g (0.005 mol) of pyridine in 20 mL of anhydrous diethyl ether was added dropwise during 10 min to a stirred solution of 1.32 g (0.005 mol) of benzyl benzenethiolsulfonate (**2b**) and 0.55 g (0.005 mol) of benzenethiol in 30 mL of anhydrous diethyl ether at 24 °C under nitrogen. The mixture was stirred for 2.5 h and washed with water and dilute $NaHCO_3$ solution. The aqueous phase was back-extracted with diethyl ether, and the combined diethyl ether solutions were dried ($MgSO_4$) and evaporated in vacuo below 30 °C to yield 1.05 g (90%) of **2**, purity ca. 95% (^1H NMR assay). Evaporative distillation[11] at 103–105 °C (bath) (0.1 mm) afforded pure **2** as a pale yellow oil [lit. bp 130–132 °C (2 mm),[9] 112 °C (0.01 mm)[10]: ^1H NMR ($CDCl_3$) δ 3.91 (s, 2) and 7.1–7.6 (m, 10); ^{13}C NMR ($CDCl_3$) δ_C 43.3 ($^{13}CH_2$) and 126.1–129.3 ($^{13}C_6H_5$).[14]

Formation of Phenyl α-Toluenethiolsulfonate (2a) by Oxidation of Benzyl Phenyl Disulfide (2) with *m*-Chloroperoxybenzoic Acid (MCPBA). A solution of 400 mg (2.0 mmol) of MCPBA (ca. 85% pure) in 10 mL of CH_2Cl_2 was added dropwise during 17 min to a stirred solution of 232 mg (1.0 mmol) of pure **2** in 8 mL of CH_2Cl_2 at −2 °C under N_2. Stirring was continued for 1 h at ca. −6 °C and for 4.5 h at 20 °C. The reaction mixture was filtered to remove insoluble *m*-chlorobenzoic acid. The filtrate was evaporated, and the residue was fractionally crystallized several times from CCl_4–diethyl ether until 250 mg of a pink solid, mp 95–104 °C, containing **2a** and some other intractable products in a ratio of 7:3, respectively, was obtained (^1H NMR assay). Recrystallization from diethyl ether gave 120 mg (45%) of pure **2a** as colorless crystals: mp 108–110 °C (lit.[7] mp 110–111 °C); ^1H NMR ($CDCl_3$) δ 4.43 (s, 2) and 7.3–7.6 (m, 10).[12]

Preparation of Phenyl α-Toluenethiolsulfonate (2a). The procedure of Kice and Engebrecht[7] was modified as follows. A solution of 1.1 g (0.010 mol) of benzenethiol in 50 mL of benzene was added dropwise to a stirred CCl_4 solution (25 mL) containing 1.9 g (0.012 mol) of Br_2 during 10 min at −10 °C. Nitrogen was bubbled through the solution for 40 min to remove the HBr which was formed. Benzene (50 mL) and a mixture of 2.0 g of α-toluenesulfinic acid[7] in H_2O (60 mL) were added to the solution. Stirring was continued for 5 min. The reaction mixture was transferred to a separatory funnel and shaken for 15 min. The aqueous phase was removed, and the benzene layer was washed with dilute $NaHCO_3$ solution and water and dried ($MgSO_4$). Removal of the solvent in vacuo afforded 2.2 g (83%) of crude **2a** which on recrystallization from Et_2O–CH_2Cl_2 yielded 1.7 g (64%) of pure **2a**: mp 109–111 °C (lit. mp 110–111,[7] 117.1 °C[13]); ^1H NMR ($CDCl_3$) δ 4.43 (s, 2) and 7.3–7.6 (m, 10); ^{13}C NMR ($CDCl_3$) δ_C 65.9 ($^{13}CH_2$) and 127.4–136.0 ($^{13}C_6H_5$).[14]

Preparation of Benzyl Benzenethiolsulfonate (2b). A solution of 3.72 g (0.030 mol) of α-toluenethiol in 150 mL of benzene was added dropwise to 100 mL of CH_2Cl_2 containing 4.8 g (0.030 mol) of Br_2. The reaction mixture was kept at −17 to −20 °C during the 20 min addition period. The deep red solution was stirred at −20 °C for 30 min longer. Nitrogen was then bubbled through the solution for 15 min. The solution was diluted with 200 mL of benzene, and a mixture of 5.0 g (0.035 mol) of benzenesulfinic acid in 150 mL of water was added to the stirred solution. The red color of the sulfenyl bromide was rapidly and completely discharged. The reaction mixture was quickly transferred into a separatory funnel, shaken for 30 min, and extracted with CH_2Cl_2. The combined organic extracts were washed with water, dilute $NaHCO_3$ solution, and brine and dried ($MgSO_4$). The solvent was removed in vacuo to give a yellow oil (7.6 g) containing **2b** and dibenzyl disulfide in a 3:1 molar ratio (^1H NMR assay). Several recrystallizations from CCl_4–hexane afforded 4.3 g (54%) of pure **2b** as colorless crystals: mp 40–42 °C (lit.[1c] 43 °C); ^1H NMR ($CDCl_3$) δ 4.27 (s, 2), 7.21 (m, 5), and 7.25–7.95 (m, 5); ^{13}C NMR ($CDCl_3$) δ_C 40.2 ($^{13}CH_2$) and 126.6–133.4 ($^{13}C_6H_5$).[14]

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Registry No.—1, 4032-81-9; **1a**, 1129-40-4; **1b**, 1127-31-7; **2**, 16601-17-5; **2a**, 37945-60-1; **2b**, 16601-01-7.

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(2) Cf. the results of peroxyacid oxidations of methyl and ethyl 2-methyl-2-propyl disulfides reported by E. Block and J. O'Connor, *J. Am. Chem. Soc.*, **96**, 3921 (1974).

(3) That such preferential oxidation may occur at the –SO– of a thiolsulfinate has already been suggested by Walter and Heil, see ref 1b, and by A. Padwa and R. Gruber, *J. Org. Chem.*, **35**, 1781 (1970).

(4) It should be noted, however, that alternate pathways from disulfides to thiolsulfonates have been suggested which include, e.g., intramolecular disproportionation of an unstable α-disulfoxide intermediate (which, incidentally, is not ruled out in the cases cited in ref 3) and/or induced disproportionation of an intermediate thiolsulfinate(s) initiated by sulfinyl radicals (RS(O)•) formed by spontaneous cleavage of a small amount of α-disulfoxide produced by direct oxidation of the intermediate thiolsulfinate(s). The latter pathway should, however, normally lead to additional thiolsulfonate products derived from scrambling of the species produced by cleavage of the S–S bond of the intermediate thiolsulfinate(s) upon attack by RS(O)• radicals. For a timely summary and some recent experimental data pertinent to this aspect of the oxidation of thiolsulfinates, see M. M. Chau and J. L. Kice, *J. Am. Chem. Soc.*, **98**, 7711 (1976). See also S. Oae, Y. H. Kim, T. Takata, and D. Fukushima, *Tetrahedron Lett.*, 1195 (1977).

(5) For those previously reported cases where at least *some* nonscrambled thiolsulfonate products were formed and examined, in two series of unsymmetrical diaryl disulfides[1a,b] oxidation appeared to occur (in the absence of steric effects) at the sulfur atom furthest removed from the relatively more electron-withdrawing substituent, in apparent agreement with our results for **1** and **2**. In another study, Walter and Heil[1b] found that peroxyacid oxidation of a series of three pyridyl alkyl disulfides gave low yields of thiolsulfonates (12, 16, and 34%) in which the alkyl-substituted sulfur had been oxidized to $-SO_2-$, as would also have been predicted by our results (assuming also, as we have, that only the –S(O)– sulfur of an intermediate thiolsulfinate is oxidized further to yield the observed thiolsulfonate). However, in contrast to our observations with **1** and **2**, where the major products (in over 65% yield) are **1a** and **2a**, the above reports also mention that considerable amounts of "scrambling" and/or "decomposition" products are simultaneously formed, especially where the oxidations of *diaryl disulfides* (ref 1a,b,d; see also ref 4) were examined, thereby indicating that at least some, and perhaps even all, of the final thiolsulfonate products observed arose from intermediate α-disulfoxides by the pathway(s) suggested in ref 4 (at least one of which has received support from Chau and Kice's data[4]). Consequently, the predictive value of these reports[1a,b,d] in terms of identifying the site(s) of initial oxidation to yield thiolsulfinate(s), as well as the structure of the major thiolsulfonate that will be finally produced, must be considered dubious.

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(11) Attempted vacuum distillation of a sample of **2**, purity ca. 95% (^{1}H NMR assay), at an oil bath temperature of 140 °C led to formation of an equimolar mixture of diphenyl disulfide and dibenzyl disulfide (^{1}H NMR assay).

(12) In the course of oxidations of **2** in which less than 2 equiv of MCPBA was consumed, the disappearance of the singlet due to the CH_2 of **2** at δ 3.91 gave rise to two new CH_2 singlets, one (due to **2a**) at δ 4.43 and another at δ 4.33; the latter decreased in intensity with corresponding increases in the intensity of the peak at δ 4.43. No characteristic sharp and intense peaks due to **2b** at δ 4.27 or 7.21 were in evidence. The peak at δ 4.33 is most probably due to phenyl α-toluenethiolsulfinate (as opposed to benzyl benzenethiolsulfinate) since no additional peaks were in evidence in the δ 7.7–8.1 region where deshielded protons ortho to an –S(O)– substituent on phenyl normally occur. For similar reasons, the peak at δ 4.33 would not seem to be attributable to an intermediate α-disulfoxide. Further evidence bearing on this latter point comes from an oxidation of **2** in which ca. 1.6 equiv of MCPBA was used, yielding a product mixture having both CH_2 singlets, as before, at δ 4.43 and 4.33; in this case no further disappearance of the singlet at δ 4.33 was observed once the *m*-chloroperoxybenzoic acid was completely consumed (as would be expected for phenyl α-toluenethiolsulfinate, but not for an α-disulfoxide which, as suggested by Chau and Kice's results[4] and those of Oae,[4] would be expected to be highly unstable). [Note that the CH_2 groups of thiolsulfinates and α-disulfoxides would not *normally* be expected to give rise to *singlets* unless accidental degeneracy exists. Thus, the thiolsulfinate from **2** could also show an AB system, and the "α-disulfoxide" could show a pair of AB systems corresponding to *RR/SS* and *RS/SR* configurations at sulfur.]

(13) Y. Abe and J. Tsurugi, *Chem. Lett.*, 441 (1972).

(14) We thank Dr. Jacob Schaefer (Central Research Division, Monsanto Co., St. Louis, Mo.) for obtaining the ^{13}C NMR spectra of **2**, **2a**, and **2b**. The ^{13}C NMR chemical shifts are reported in δ (ppm) downfield from Me_4Si, based on $\delta(Me_4Si) = \delta(CDCl_3) - 77.0 = 0.0$ ppm.

The Resorcinol–Maleic Anhydride Condensation Product. An Unequivocal Proof of Structure

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No less than four structures have been proposed for the crystalline product formed on condensation of resorcinol with maleic anhydride in the presence of zinc chloride or concentrated sulfuric acid. Two of these structures, namely bis-(2′,4′-dihydroxyphenyl)but-2-en-1,4-dione[1] and 4,4-bis(2′,4′-dihydroxyphenyl)but-2-en-4-olide[2] are untenable on the basis of the NMR spectrum whereas the isomeric γ-lactone 1[3] and δ-lactone 2[4] structures are indistinguishable by this or other spectrometric methods. Unequivocal structural proof by chemical methods was therefore essential.

Methylation of the phenolic condensation product[3] or its triacetate[4] yielded a tetramethyl ether methyl ester **3**, R = Me, or **4**, R = Me, but assignment of either one or the other of these structures to this compound was not possible from the spectroscopic evidence. Although both esters **3**, R = Me, and **4**, R = Me, had been obtained previously[5] by Friedel–Crafts condensation of resorcinol dimethyl ether with 2,4-dimethoxyphenylsuccinic anhydride followed by esterification and structural assignments made on analogical arguments, the formation of both isomers in the same reaction precludes such assignments in the absence of more definitive evidence.

Structure **4**, R = Me, for the tetramethyl ether methyl ester was initially supported by comparison of the NMR spectrum with that of its oxime. Thus, the methine proton exhibited a 43-ppm upfield shift on oximation, whereas one of the methylene protons showed an upfield shift of 28 ppm and the other a downfield shift of 14 ppm. In contrast, oximation of an ester having structure **3**, R = Me, would be expected to show a more pronounced effect upon the methylene protons compared to the methine proton, although such shifts would be sensitive to stereochemistry.

However, hydrolysis of the ester to the free acid and reduction of this compound with sodium borohydride provided unequivocal chemical evidence in favor of structure **3**. The crystalline reduction product, mp 121–2 °C, analyzed for $C_{20}H_{22}O_6$, showed a strong lactone carbonyl band at 1770 cm^{-1} in the infrared spectrum and exhibited a strong peak in the mass spectrum at *m/e* 314 due to expulsion of CO_2 from the molecular ion. The NMR spectrum indicated the presence of two 2,4-dimethoxyphenyl groups and a strongly coupled 4-spin system. The product must therefore be either 2,4-bis(2′,4′-dimethoxyphenyl)-γ-butyrolactone (**5**) or 3,4-bis(2′,4′-dimethoxyphenyl)-α-butyrolactone (**6**) which would result from lactonization of the secondary alcohol initially produced on reduction of the acids **3**, R = H, or **4**, R = H, respectively. Further analysis of the NMR spectrum readily distinguished between the isomeric lactones **5** and **6** since the high-field methylene proton signals occurred as a multiplet at δ 2.30 and a multiplet at δ 2.92, whereas the benzylic methine protons appeared as double doublets at δ 4.05 and 5.74. The reduction product is therefore the 2,4-disubstituted lactone **5**, the magnitude of the coupling constants indicating