of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

**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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(1) For example, see (a) G. Leandri and A. Tundo, *Ric. Sci.*, **23**, 1646 (1953); *Chem. Abstr.*, **48**, 12699 (1954); *Ann. Chim. (Rome)*, **44**, 74 (1954); (b) W. Walter and P.-M. Heil, *Justus Liebigs Ann. Chem.*, **727**, 50 (1969); (c) S. Hayashi, M. Furukawa, J. Yamamoto, and K. Hamamura, *Chem. Pharm. Bull.*, **15**, 1310 (1967); (d) G. Stájer, E. A. Szabó, J. Pintye, F. Klivényi, and P. Sohár, *Chem. Ber.*, **107**, 299 (1974).

(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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(10) D. A. Armitage, M. J. Clark, and C. C. Tso, *J. Chem. Soc., Perkin Trans. 1*, 680 (1972).

(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.]

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(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

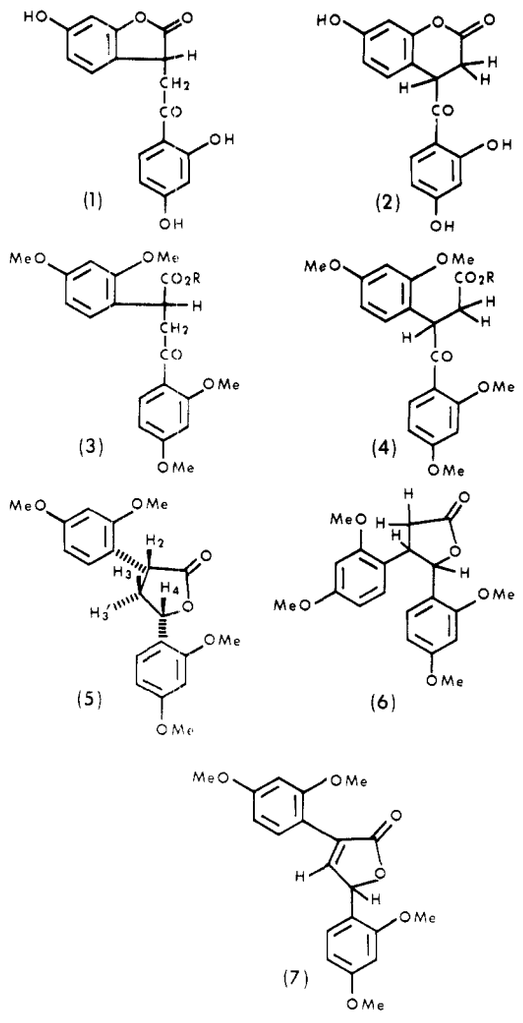


Figure 1.

the cis configuration, as determined for related δ-butyrolactones.[6]

The precursor of the latter is thus the acid **3**, R = H, which on heating under reflux in acetic anhydride gave the dehydro derivative of the lactone **5**, namely 2,4-bis(2′,4′-dimethoxyphenyl)but-2-en-4-olide (**7**). The infrared spectrum of the latter showed the expected α,β-unsaturated lactone carbonyl band at 1750 $cm^{-1}$, while the NMR spectrum exhibited doublets due to the $H_3$ and $H_4$ protons at δ 7.87 and 6.33 ($J$ = 2 Hz),[7] respectively.

The synthesis of the lactones **5** and **7** via the acid **3**, R = H, and its corresponding ester **3**, R = Me, from the resorcinol–maleic anhydride condensation product therefore unequivocally establishes the structure of the latter as 3-(2′,4′-dihydroxybenzoylmethyl)-6-hydroxybenzofuran-2-one (**1**).

## Experimental Section[8]

Melting points are uncorrected. The $^1H$ NMR spectra were obtained with a Varian HA-100 spectrometer in $CDCl_3$ solution. Infrared spectra were recorded with a Perkin-Elmer Model 237B spectrophotometer in $CHCl_3$ solution.

**Methyl 2,4-Bis(2′,4′-dimethoxyphenyl)-4-oxobutyrate Oxime.** The ester **3**, R = Me (0.5 g), hydroxylamine hydrochloride (1.0 g), and NaOAc (1.0 g) were heated together at 100 °C in 50% aq EtOH (40 mL) for 1 h. The mixture was poured into $H_2O$ and the precipitated solid was filtered off and recrystallized from aqueous MeOH as white prisms: mp 139–141 °C; NMR δ 3.29 (dd, $J$ = 14, 9 Hz, 1 H, $CH_2$), 3.52 (dd, $J$ = 14, 6 Hz, 1 H, $CH_2$), 4.16 (dd, $J$ = 9, 6 Hz, 1 H, CH), 3.55 (s, 3 H, $OCH_3$), 3.62 (s, 3 H, $CO_2CH_3$), 3.77 (s, 3 H, $OCH_3$), 3.78 (s, 6 H, 2 × $OCH_3$), 6.24–6.54 (m, 4 H, ArH), 6.76 (d, $J$ = 8 Hz, 1 H, ArH), 7.05 (d, $J$ = 8 Hz, 1 H, ArH). Anal. Calcd for $C_{21}H_{25}NO_7$: C, 62.5; H, 6.25; N, 3.47. Found: C, 62.6; H, 6.32; N, 3.44.

**2,4-Bis(2′,4′-dimethoxyphenyl)-γ-butyrolactone (5).** The acid **3**, R = H (1.5 g), in MeOH (100 mL) was treated with $NaBH_4$ (2.0 g), added in portions, and the solution was stirred at room temperature overnight. The mixture was poured into $H_2O$ and the precipitated solid was filtered off, washed, air dried, and recrystallized from MeOH as white needles (0.6 g), mp 119–121 °C. The aqueous solution was extracted with $Et_2O$, acidified with dilute hydrochloric acid, and extracted with $CHCl_3$. The extract was washed, dried, and evaporated and the residue was recrystallized from MeOH to give a further quantity of the lactone (0.75 g): mp 119–121 °C; IR 1770 $cm^{-1}$ (lactone C=O); NMR δ 2.30 (m, $J_{2,3\beta}$ = 12.5, $J_{3\beta,4}$ = 10.5, and $J_{3\alpha,3\beta}$ = 13.0 Hz, 1 H, H-3 β), 2.92 (m, $J_{2,3\alpha}$ = 9.0, $J_{3\alpha,4}$ = 6.0 Hz, and $J_{3\alpha,3\beta}$ = 13.0 Hz, 1 H, H-3α), 3.80 (s, 6 H, 2 × OMe), 3.82 (s, 6 H, 2 × OMe), 4.05 (q, $J_{2,3\alpha}$ = 9.0, $J_{2,3\beta}$ = 12.5 Hz, 1 H, $H_2$), 5.74 (q, $J_{3\alpha,4}$ = 6.0, $J_{3\beta,4}$ = 10.5 Hz, 1 H, $H_4$), 6.38–6.60 (m, 4 H, ArH), 7.11 (d, $J$ = 9 Hz, 1 H, ArH), 7.42 (d, $J$ = 8 Hz, 1 H, ArH); MS $m/e$ 358 ($M^+$), 314 ($M - CO_2$). Anal. Calcd for $C_{20}H_{22}O_6$: C, 67.04; H, 6.15. Found: C, 67.1; H, 6.19.

**2,4-Bis(2′,4′-dimethoxyphenyl)but-2-en-4-olide (7).** The acid **3**, R = H (0.75 g), in $Ac_2O$ (10 mL) was heated under reflux for 3 h[6] and the solution was allowed to cool and was poured into ice–water. The precipitate was filtered off, washed with $H_2O$, air dried, and recrystallized from $Me_2CO$–MeOH as pale yellow prisms: mp 150–151 °C (0.5 g); IR 1750 $cm^{-1}$ (α,β-unsaturated lactone C=O); NMR δ 3.81 (s, 3 H, OMe), 3.84 (s, 6 H, 2 × OMe), 3.87 (s, 3 H, OMe), 6.32 (d, $J$ = 2 Hz, 1 H, $H_4$), 6.38–6.63 (m, 4 H, ArH), 7.11 (d, $J$ = 9 Hz, 1 H, ArH), 7.87 (d, $J$ = 2 Hz, 1 H, $H_3$), 8.26 (d, $J$ = 8 Hz, 1 H, ArH). Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66. Found. C, 67.4; H, 5.63.

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**Registry No.**—**1**, 15833-58-6; **3** (R = Me), 15833-60-0; **3** (R = Me) oxime, 66239-92-7; **3** (R = H), 66239-93-8; **5**, 66239-94-9; **7**, 66239-95-0; resorcinol, 108-46-3; maleic anhydride, 103-31-6.

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# Facile Reaction of Alcohols and Phenols with Borane–Methyl Sulfide. A New, General, and Convenient Synthesis of Borate Esters

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In our exploratory studies involving the synthesis and reduction characteristics of alkoxyborohydrides,[1] we required a simple and direct route to alkyl and aryl borates of varying structures, applicable to preparation of fractional molar quantities.

Existing routes of borate esters[2] can be broadly classified into three types: (1) direct esterification of boric acid or anhydride with azeotropic distillation of water; (2) transesterification with a low boiling borate (usually methyl or ethyl borate); and (3) reaction of sodium borohydride with acetic acid in the presence of excess alcohol (eq 1).

$$NaBH_4 + CH_3COOH + ROH \text{ (excess)} \rightarrow CH_3COONa + B(OR)_3 + 4H_2\uparrow \quad (1)$$

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