Solvents and Materials. Absolute EtOH (U.S. Industrial Chemicals), HPLC-grade water, and Hg (Alfa, electronic grade) were used as received to prepare electrolysis reaction mixtures. *meso*-**2** [mp 159–160 °C (lit.[11] mp 163.5–164 °C)] and (*E*)-4-phenyl-3-buten-2-ol [mp 36-38 °C (lit.[12] mp 35–36 °C)] were prepared by literature procedures.[3a,13] The materials below were obtained from Aldrich, except for $NaDodSO_4$ (BDH, specially pure). HTABr, $NaDodSO_4$, and Brij 35 were purified by literature procedures.[14] Me_4NBr (mp >300 °C) and Bu_4NBr (mp 115–117 °C) were recrystallized from MeOH (5 °C). **1** was recrystallized from hexane (−5 °C) with Norit treatment (mp 39.5–40 °C). **3** [bp 116–118 °C (ca. 20 mmHg)] and PhCOMe (bp 191–192 °C) were distilled. 4-Phenyl-2-butanol and *n*-butylbenzene were used as received.

Electrolysis Apparatus. A Princeton Applied Research Model 173 potentiostat/galvanostat was used for controlled-potential electrolyses, which were performed in a jacketed, cylindrical 90-mL glass cell (4.7-cm diameter) fitted with a Teflon lid containing a central opening (5 mm diameter) and five peripheral openings (8 mm diameter). A glass stirrer was inserted through the former, and the latter provided access for the anode (Ag/AgBr) and reference electrode (SCE) compartments, a N_2 tube, and an electrical connection to the Hg cathode at the bottom of the cell. Before introduction into the reaction mixture, purified N_2 was passed through a gas-washing bottle containing the same solvent used in a given electrolysis.

Electrolysis Procedure and Analysis. For entry 3, 20 mL each of EtOH and pH 5.1 0.250 M NaOCOMe–$MeCO_2H$ buffer was mixed, followed by the addition of 412 mg (4.00 mmol) of NaBr, to give a solution containing 0.100 M NaBr and total μ = 0.225. The reaction media for the other entries were prepared similarly. To the above cell thermostated at 25.0 ± 0.1 °C was added ca. 10 mL of Hg and 40 mL of the reaction solvent. Stirring and the N_2 flow were begun and continued throughout the experiment. After 15 min, the solvent was preelectrolyzed at −1.60 V (vs. SCE) for 1 h. After 58.5 mg (0.400 mmol) of powdered **1** was added and dissolved (taking up to 15 min in micellar media), the reaction mixture was electrolyzed for 2 h. Then, 51.0 mg (0.425 mmol) of PhCOMe was added as internal standard, and a sample of the mixture was filtered (Millipore HV, 0.45 μm) and analyzed by calibrated HPLC at 220 nm. The results are summarized in Table I; the yields are averages of at least duplicate runs. In general, little or no **1** remained at the end of an electrolysis. A different sample of Hg was used for each medium, and after every electrolysis, it was washed successively with three 25-mL portions each of EtOH, H_2O, and EtOH and filtered through a filter paper funnel containing a pin hole.

Polarography. Differential-pulse polarography was performed with a Princeton Applied Research Model 174A polarographic analyzer. A dropping Hg electrode, a Pt wire anode, and a SCE reference electrode with a 0.2 M Na_2SO_4 bridge were used. The scan range was −0.80 to −1.60 V, the scan rate was 2 mV/s, and the drop rate was 0.5 s. The sample was degassed with Ar.

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Registry No. **1**, 1896-62-4; **2**, 7028-44-6; **3**, 2550-26-7; HTABr, 57-09-0; $NaDodSO_4$, 151-21-3; Brij, 9002-92-0; Na^+, 17341-25-2; K^+, 24203-36-9; Me_4N^+, 51-92-3; Bu_4N^+, 10549-76-5.

Supplementary Material Available: Detailed descriptions of the electrolysis cell and the HPLC analyses, including retention times and calibration factors (1 page). Ordering information is given on any current masthead page.

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A Facile Access to (*R*)-Malic Acid

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Of the two enantiomeric malic acids, the (*R*) isomer has been considered to be the more difficultly accessible, hence its higher cost. As a result of this situation, several syntheses of (*R*)-malic acid or its immediate derivatives have been published within the last few years. Thus, Seebach and co-workers[1] have transformed (*R*,*R*)-dimethyl tartrate into (*R*)-dimethyl malate in four steps and 44% overall yield. Wynberg and Staring[2] produced the optically pure acid in 79% overall yield by application of a remarkable asymmetric cycloaddition catalyzed by quinidine. A very recent report[3] describes the synthesis of enantiomerically pure (*R*)-malic acid from (*R*)-aspartic acid in three steps and 68% overall yield.

We describe herein a simple and expedient synthesis of (*R*)-dimethyl malate (**3**) from (*R*,*R*)-dimethyl tartrate (**1**) in two steps and 67% overall yield (Scheme I). Thus, **1** was transformed into the corresponding crystalline thionocarbonate derivative **2** in 76% yield. Treatment of **2** with tri-*n*-butyltin hydride[4] gave (*R*)-dimethyl malate (**3**) in 88% yield after purification by flash chromatography. The optical purity of **3** was ascertained by comparison of its chiroptical properties with reported constants for pure material.[1,3,5] The transformation of **3** into optically pure (*R*)-malic acid has already been reported.[2]

Experimental Section

(4*R*,5*R*)-2-Thioxo-4,5-bis(methoxycarbonyl)-1,3-dioxolane (2). To a stirred solution of (2*R*,3*R*)-dimethyl tartrate (**1**)[6] [[α]^{25} −8° (*c* 5.83, $CHCl_3$); 3.56 g, 20 mmol] in THF (80 mL) was added a solution of thiocarbonyldiimidazole[7] (3.56 g, 20 mmol) in THF (80 mL) dropwise over 15 min under argon, and the resulting yellow solution was stirred for 2 h at room temperature. The solution was concentrated under reduced pressure to one-third its initial volume, ether (300 mL) was added, and the resulting solution was washed consequtively with HCl (100 mL), water (100 mL), saturated bicarbonate (50 mL), and water again. Processing the organic phase in the usual manner and removal of the solvent gave the thionocarbonate derivative **2** as a light yellow oil that crystallized on standing; yield 3.35 g (76%). A sample was purified by flash chromatography[8] for analytical purposes (hexane–ethyl acetate, 2:1): mp 59–60 °C; [α]$^{25}_D$ −45° (*c* 11.5, $CHCl_3$); MS, *m/e* 221 (M + 1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 (3 H, s), 5.38 (1 H, s); IR (KBr) 1750, 1435, 1375 cm^{-1}. Anal. Calcd for $C_7H_8O_6S$: C, 38.18; H, 3.66; S, 14.56. Found: C, 38.11; H, 3.64; S, 14.42.

(*R*)-Dimethyl Malate (3). A solution containing **2** (2 g, 9.08 mmol) and tri-*n*-butyltin hydride (2.69 mL, 10 mmol) was refluxed under argon for 20 min. After the mixture was allowed to cool to room temperature, 50 mL of methanol and 6 g of silica were added. The mixture was stirred for 2 h, the solvent was removed under reduced pressure, and the residue was purified by flash chromatography (*n*-hexane, then hexane–ethyl acetate gradient, 1:1). The desired fractions were evaporated, and the residue was partitioned between acetonitrile and *n*-hexane. The lower layer was processed as usual to give the title product as a colorless oil: yield 1.3 g (88%); [α]$^{25}_D$ 6.2° (neat) [lit.[1] [α]$_D$ 6.4°]; [α]$^{25}_D$ 9.5°

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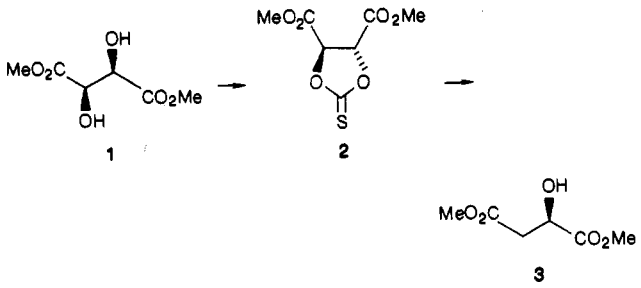
Scheme I



1 2 3

(c 2.5, EtOH) [lit.[5] $[\alpha]_D$ 9.1° (c 2.2, EtOH)]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (1 H, dd, J = 6.1 and 16.4 Hz, $CH_3OOCCH_aH_bCHOHCOOCH_3$), 2.87 (1 H, dd, J = 4.4 and 16.4 Hz, $CH_3OOCCH_aH_bCHOHCOOCH_3$), 3.20 (1 H, d, J = 5.4 Hz, $CH_3OOCH_aH_bCHOHCOOCH_3$), 3.72 and 3.82 (6 H, 2 s, $CH_3OOCCH_aH_bCHOHCOOCH_3$), 4.51 (1 H, m, $CH_3OOCCH_2CHOHCOOCH_3$).

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Role of the *p*-Hydroxyl Group in the Nitrobenzene Oxidation of Hydroxybenzyl Alcohols

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For nearly half a century, the alkaline nitrobenzene oxidation of lignin[1,2] has been used to convert lignin to identifiable mixtures of aromatic aldehydes and, to a lesser extent, aromatic acids. The generally accepted mechanism for this oxidation is a heterolytic process involving a quinone methide intermediate.[3] Recent findings[4] suggest that a homolytic oxidative–cleavage mechanism better describes this reaction. This new mechanism is formally similar to that observed by Trahanovsky[5,6] in the ceric ammonium nitrate oxidation of 1,2-diarylethanols. Furthermore, Ashby[7] has found ESR evidence that the Cannizzaro reaction, which is a side reaction in the nitrobenzene oxidation, may also be homolytic in nature. Also, the hemoprotein ligninase of *Phanerochaete chrysosporium* has recently been found[8] to catalyze the one-electron oxidation of methoxybenzene lignin model compounds forming cation radical intermediates that eventually demethylate to quinone products.

The claim has frequently been made[3,9] that a *p*-hydroxyl group is required on a lignin model compound for the nitrobenzene oxidation to work. The function of the *p*-hydroxyl group was believed to be threefold: (a) to impart aqueous alkali solubility to the compound, (b) to protect the aldehyde product from the Cannizzaro side reaction, and (c) to facilitate the formation of a quinone methide intermediate. We have reason to question the last function.

The necessary *p*-hydroxyl claims are based on some methylation studies. When a series of about a dozen C_3 arene compounds also containing either 4-hydroxy-3-methoxy or 3,4-dimethoxy substituents were subjected to the nitrobenzene oxidation reaction, only the compounds with the 4-hydroxy-3-methoxy substituents gave appreciable amounts of aldehydes.[9,10] Leopold[11] methylated various lignins with diazomethane (methylation of phenolic OH's) and found that the yield of vanillin from the nitrobenzene oxidation of these methylated lignins decreased by 15–20%. Further methylation by dimethyl sulfate[12] (all OH's methylated) resulted in a 70% decrease in vanillin product. These methylation studies clearly show that benzylic hydroxyl groups in lignin are more important in vanillin formation than are *p*-hydroxyl groups.

In this study the kinetics and activation parameters of the alkaline nitrobenzene oxidation of *p*-hydroxybenzyl alcohol (1), *m*-hydroxybenzyl alcohol (2), and 4-hydroxy-3-methoxybenzyl alcohol (3) were studied as lignin model compounds. The compounds were chosen to test the necessity of a *p*-hydroxyl group in its presumed role of acting as a precursor for the formation of a quinone methide intermediate.

Results and Discussion

Kinetics. In an earlier study,[4] the nitrobenzene oxidation of *o*-, *m*-, and *p*-hydroxybenzyl alcohols at 150 °C for 1 h was found to give the corresponding hydroxybenzaldehydes in 14, 47, and 51% yields, respectively. Compound 3, also called vanillyl alcohol, gives vanillin in 70% yield under the same conditions. The aldehyde yields can be improved by longer reaction times, but side reactions also become increasingly important with time. Under the conditions used in these kinetic runs, 1, 2, and 3 gave 60–75% oxidation to the corresponding benzaldehydes. *o*-Hydroxybenzyl alcohol was the only one of this series that gave a poor yield of aldehyde and, for this reason, its kinetics were not studied. The pseudo-first-order rate constants and activation parameters for the oxidations of 1, 2, and 3 are given in Table I.

A 16-fold excess of nitrobenzene over hydroxybenzyl alcohol was used in each reaction to simplify the kinetics by removing nitrobenzene dependence from the rate law and also to approximately duplicate the nitrobenzene excess normally used in the oxidation of lignin. The result was that both the disappearance of alcohol and the appearance of aldehyde followed pseudo-first-order kinetics. These kinetics were, however, further complicated by side reactions.

Benzyl alcohols 1 and 3, both of which contain a *p*-hydroxyl group, each undergo a competing self-condensation reaction under the strongly basic conditions of the reaction. The reaction of 1 with dilute NaOH has been

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