of two isomers in a 1:1.1 ratio (^{1}H NMR). The material was recrystallized from ether–dichloromethane: mp 141–142 °C; FT-IR (Nujol) 3509, 3487, 1744, 1447, 1377, 1318, 1302, 1292, 1180, 1146, 1084, 1073, 738, 727, 585, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.10–1.96 (m, 9.5 H), 2.30 (m, 2.0 H), 2.62 (qd, J = 1.5, 6.5, 13.5 Hz, 0.5 H), 3.84 (dd, J = 8.5, 9.5 Hz, 0.51 H), 4.12 (dd, J = 1.5, 9.7 Hz, 0.46 H), 7.59 (m, 2 H), 7.69 (m, 1 H), 7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 20.3, 24.2, 24.3, 25.2, 25.4, 26.8, 27.0, 30.3, 30.4, 42.6, 43.6, 66.9, 68.8, 75.7, 76.5, 129.0, 129.1, 129.2, 134.0, 134.1, 134.2, 137.8, 138.6, 202.3, 203.5; exact mass, m/z [(M – CO)$^+$] calcd for $C_{14}H_{18}O_3S$ 266.0977, found 266.0975. Anal. Calcd for $C_{15}H_{18}O_4S$: C, 61.20; H, 6.16. Found: C, 61.08; H, 6.15.

(7a*R,3a*R**)-Octahydro-7a-hydroxy-1-oxo-2-(phenylsulfonyl)-1-*H*-indene (16d) and (7a*R**,3a*S**)-Octahydro-7a-hydroxy-1-oxo-2-(phenylsulfonyl)-1-*H*-indene (16d').** The procedure for **17d** was followed using alkenes **16c** and **16c'** (237.0 mg, 643.2 mmol) in 5:1 dichloromethane–methanol (25 mL). Flash chromatography of the crude product over silica gel (2 × 15 cm) using 25% ethyl acetate–hexane afforded two solids, which were each a chromatography (TLC) inseparable mixture of two isomers (^{1}H NMR), together with cis ring-fused unreacted starting material (49.9 mg, 21%). The material of higher R_f 51.1 mg, 27% yield; 34% based on conversion) was recrystallized from ether–dichloromethane and identified as the trans ring-fused ketones **16d** in a 1:1.1 ratio that had *not* been altered (^{1}H NMR) by crystallization: mp 140–145 °C; FT-IR (MeOH) 1752, 1307, 1147, 1084 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.09–1.95 (m, 9.5 H), 2.30 (m, 2 H), 2.62 (qd, J = 1.5, 6.5, 13.5 Hz, 0.5 H), 3.82 (dd, J = 8.5, 9.5 Hz, 0.55 H), 4.12 (dd, J = 1.5, 9.7 Hz, 0.45 H), 7.59 (m, 2 H), 7.69 (m, 1 H), 7.90 (m, 2 H); ^{13}C NMR ($CDCl_3$, 75.5 MHz) δ 20.4, 20.4, 24.3, 24.4, 25.3, 25.4, 26.8, 27.1, 30.3, 30.4, 42.7, 43.6, 67.0, 68.9, 75.8, 129.1, 129.1, 129.1, 129.2, 134.1, 134.3; exact mass, m/z [(M – CO)$^+$] calcd for $C_{14}H_{18}O_3S$ 266.0976, found 266.0975.

The compound of lower R_f (75.6 mg, 40% yield; 50% based on conversion) was identified as the cis ring-fused materials **16d'**: mp 120–150 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.16–2.46 (m, 11.65 H), 2.74 (m, 0.35 H), 3.99 (m, 1 H), 7.60 (m, 2 H), 7.70 (m, 1 H), 7.90 (m, 2 H); exact mass, m/z [(M – CO)$^+$ calcd for $C_{14}H_{18}O_3S$ 266.0976, found 266.0975.

Octahydro-7a-hydroxy-1-oxo-1-*H*-indene (16e). The general literature procedure[26] was followed. Three strips of aluminum foil (1 × 5 cm) were dipped into a 2% w/v aqueous solution of mercurous chloride for 15 s, then into 95% ethanol, and finally into ether. The strips were immediately cut into 0.5-cm square pieces and dropped into a stirred solution of sulfones **16d** and **16d'** (30.8 mg, 0.105 mmol) in 10% aqueous THF (10 mL). Stirring was continued for 6 h, and the mixture was then refluxed for 3 h, cooled, filtered, and evaporated. The resulting oil was dissolved in dichloromethane, and the solution was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1 × 15 cm) using 25% ethyl acetate–hexane afforded unreacted starting material (8.0 mg, 25%) and **16e** (12.0 mg, 74%; 98% based on conversion). Compound **16e**: FT-IR (CCl_4 cast) 3420, 1742, 1710, 1442 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.78–2.58 (series of multiplets); ^{13}C NMR ($CDCl_3$, 300 MHz) δ 20.7, 24.2, 24.7, 24.9, 25.1, 25.8, 28.1, 30.5, 31.4, 34.2, 35.1, 42.2, 45.9, 49.7, 75.1, 216.6; exact mass, m/z calcd for $C_9H_4O_2$ 154.0994, found 154.1000.

Supplementary material available: Crystal structure data (23 pages) for **17c** available from the authors.

Acknowledgment of financial support is made to the Natural Sciences and Engineering Research Council of Canada. We thank Dr. R. Ball of this department for the X-ray structure determination.

Structural and Solvent/Electrolyte Effects on the Selectivity and Efficiency of the Anodic Oxidation of Para-Substituted Aromatic Ethers. An Efficient Route to Quinol Ether Ketals and Quinol Ethers

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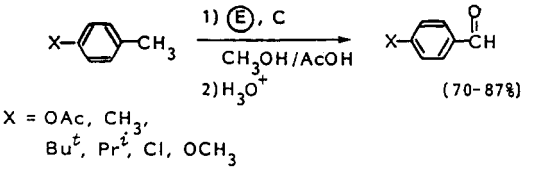
The anodic oxidations of the methyl ethers of *p*-arylphenols [*p*-aryl = C_6H_5, *o*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, *o*-[$(CH_3)_2$-*t*-BuSiOCH_2]C_6H_4, *o*-[$(H_3CO)_2HC$]C_6H_4, *o*-$HO_2CC_6H_4$], the 2-hydroxyethyl ethers of *p*-arylphenols [*p*-aryl = C_6H_5, *o*-$CH_3C_6H_4$, *p*-$CH_3OC_6H_4$, 3,4-$(CH_3O)_2C_6H_3$, 2-thiopheneyl], and the 2-hydroxyethyl ethers of *p*-alkylphenols [*p*-R = CH_3, C_2H_5, *i*-C_3H_7, *t*-C_4H_9] and 4-methyl-1-naphthol were studied. The *p*-aryl aromatic ethers underwent anodic oxidation in good yield to give the corresponding *p*-quinol ether ketals. The ratio of nuclear to side-chain products from anodic oxidation of *p*-alkylanisole derivatives is dependent upon the electrolysis conditions. The 2-hydroxyethyl ether derivatives of *p*-alkylphenols markedly favor the formation of nuclear oxidation products—providing a useful route to the corresponding *p*-quinol ether ketals. In addition, methanolic potassium fluoride improves the efficiency of these anodic oxidation processes by about 400% relative to methanolic potassium hydroxide. These reactions were performed at a constant current (1.0–2.0 A) in a single cell and serve as preparative routes to *p*-quinol ether ketals and quinol ethers via acid hydrolysis.

Introduction

The anodic oxidation of aromatic compounds in methanol often serves as a general route for the preparation of quinone bisketals.[1,2] Although 1,4-dimethoxy aromatic compounds are most often used for the oxidation, benzene,[3] monomethoxylated aromatic compounds,[4,5] and heterocyclic ring systems[5] have also been successfully em-

Scheme I. Side-Chain Oxidation of Para-Substituted Toluenes

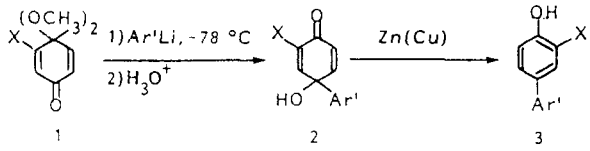


(1) Swenton, J. S. *Acc. Chem. Res.* **1983**, *16*, 74 and references cited therein.

(2) (a) Weinberg, N. L.; Belleau, B. *J. Am. Chem. Soc.* **1963**, *85*, 2525. (b) Henton, D. R.; McCreery, R. L.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 369. (c) Henton, D. R.; Anderson, D. K.; Manning, M. J.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 3422.

0022-3263/87/1952-4953$01.50/0

Table I. Preparation of 4-Hydroxybiphenyls



1 2 3

	Ar'	% yield 2	% yield 3
a	C_6H_5	78	83
b	o-$CH_3C_6H_4$	76	66
c	p-$CH_3OC_6H_4$	78	76
d	3,4-$(CH_3OC_6H_3)_2$		50[a]
e	2-thiopheneyl	*b*	72
f	C_6H_5	70[c]	81[c]

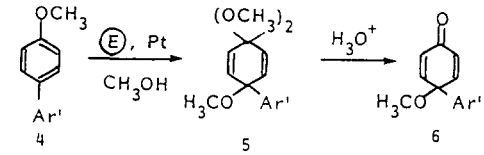
[a] Overall yield from 1. [b] Yield of p-quinol ketal was 59%. [c] X = H except for **1f** in which X = OCH_3.

ployed as starting materials. These quinone bisketals can usually be converted in high yield to synthetically versatile quinone monoketals.[1] In contrast to the extensive investigations of anodic oxidations to form quinone bisketals, less attention has been focused on the oxidations of p-aryl[6] and p-alkyl[4,7] aromatic ethers. Undoubtedly, the known competition between nuclear and side-chain oxidation in the anodic oxidation of p-methylanisole (vide infra) has discouraged its use in the preparation of p-quinol derivatives.[4,7] However, reaction conditions can influence the ratio of side-chain to nuclear oxidation.[4,7,8] For example, the anodic oxidation of para-substituted toluenes was recently reported to afford good yields of the corresponding aldehydes after acid hydrolysis of the reaction mixtures (Scheme I).[8]

The utility of quinone bisketals and monoketals in the preparation of functionalized quinones and substituted aromatic derivatives[1] suggests p-quinol derivatives could similarly be employed in the preparation of various aryl- and alkyl-substituted aromatic systems. Thus, the anodic oxidations of a series of p-aryl and p-alkyl aromatic ethers were investigated with the objective of defining electrolysis conditions that would favor high-yield formation of p-quinol ether ketals.[9] These products could then be converted via acid hydrolysis to the respective p-quinol derivatives.

We report herein the preparative anodic oxidation studies of a series of p-aryl and p-alkyl aromatic ethers. These anodic oxidations provide a facile route to p-quinol ether ketals that can be converted to p-quinol ethers by acid hydrolysis. A key aspect of this work involved the use of 2-hydroxyethyl aromatic ethers as substrates for the oxidation. This particular ether moiety generally improved the current efficiency and afforded good yields of nuclear oxidation products from anodic oxidation of p-alkyl substituted aromatic ethers.

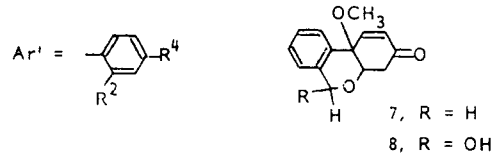
Table II. Anodic Oxidations of 4-Methoxybiphenyls



4 5 6

	R^2	R^4	% yield 5	% yield 6
a	H	H	74	74
b	CH_3	H	71	83
c	H	OCH_3	76	83
g	CH_2OSi-t-$Bu(CH_3)_2$	H	86	*a*
h	$CH(OCH_3)_2$	H	82	*b*
i	CO_2H	H	*c*	*c*

[a] **7** was obtained in 53% yield. [b] **8** was obtained in 70% yield. [c] See the text.



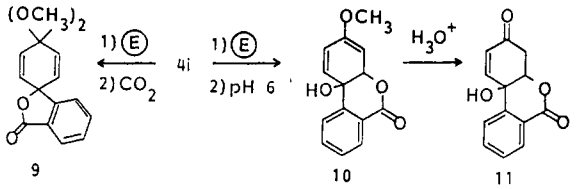
Anodic Oxidations of p-Aryl Aromatic Ether Derivatives

The first systems studied were p-arylanisole derivatives (4-methoxybiphenyls),[10] since complications from side-chain oxidation of aliphatic substituents would be absent. The required biphenyl systems were prepared by standard methods as detailed in the Experimental Section. An especially useful route to some of the biphenyls was the addition of aryllithium reagents to quinone monoketal **1** in tetrahydrofuran at −78 °C, acid hydrolysis of the resulting p-quinol ketals to the respective p-quinols, reduction, and methylation to afford the required 4-methoxybiphenyls in good overall yields (Table I). The organolithium addition was not complicated by reduction via electron-transfer reactions when conducted at −78 °C, nor was competing dienone–phenol rearrangement a problem in the acid hydrolysis step. Since substituted quinone monoketals are readily available and aryllithium reagents can be prepared via either metal–halogen exchange or metalation processes, this reaction sequence provides an efficient and convergent route to p-quinols **2** and biphenyls **3**.

The anodic oxidations of the biphenyl systems **4a–c,g,h** were conducted in a single-cell apparatus at a constant current (0.4–2.0 A) in 1% methanolic potassium hydroxide as the solvent/electrolyte system using a platinum anode. The oxidation was monitored by UV spectroscopy or thin-layer chromatography and upon completion, conventional workup, and purification by flash column chromatography on neutral alumina (activity III) afforded the corresponding phenyl-substituted p-quinol ether ketals **5a–c,g,h** in good to excellent yields (Table II). The alcohol and aldehyde functionalities in systems **4g,h**, respectively, were protected, since anodic oxidation of the unprotected systems gave complicated reaction mixtures. It was not

(3) Pistorius, R.; Mallanuer, H. U.S. Patent 4 046 652, 1975.
(4) (a) Nilsson, A.; Palmquist, U.; Pettersson T.; Ronlân, A. *J. Chem. Soc., Perkin Trans. 1* **1978**, 708. (b) Dolson, M. G.; Swenton, J. S. *J. Am. Chem. Soc.* **1981**, *103*, 2361.
(5) Chenard, B. L.; McConnell, J. R.; Swenton, J. S. *J. Org. Chem.* **1983**, *48*, 4312.
(6) DeSchepper, R. E.; Swenton, J. S. *Tetrahedron Lett.* **1985**, *26*, 4831.
(7) Torii, S.; Siroi, T. *Yuki Gosei Kagaku Kyokaishi* **1979**, *37*, 914 and references cited therein.
(8) Nishiguchi, I.; Hirashima, T. *J. Org. Chem.* **1985**, *50*, 539.
(9) For preliminary reports describing some of this work, see: (a) Reference 6. (b) Capparelli, M. P.; DeSchepper, R. E.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1987**, 610.
(10) Several papers have reported limited studies of the anodic oxidations of biphenyls. For examples, see: (a) Yoshida, K. *Electrooxidation in Organic Chemistry*; Wiley: New York, 1984; pp 126–156. (b) Sainsbury, M. *Tetrahedron* **1980**, *36*, 3338–3347. (c) Rifi, M. R. *Tetrahedron Lett.* **1969**, 5089. (d) Ronlân, A.; Coleman, J.; Hammerich, O.; Parker, V. D. *J. Am. Chem. Soc.* **1974**, *96*, 845. (e) Kenner, G. W.; Murray, M. A.; Tylor, C. M. B. *Tetrahedron* **1957**, *1*, 259. (f) Eberson, L.; Nyberg, K. *J. Am. Chem. Soc.* **1966**, *88*, 1686. (g) Jönsson, L.; Wistrand, L.-G. *J. Org. Chem.* **1984**, *49*, 3340.

essential to protect the carboxyl group of **4i**; however, the product obtained was dependent upon the workup conditions. Neutralization of the reaction mixture with carbon dioxide gave **9** as the major product. However, concentration of the basic reaction mixture followed by careful acidification afforded **10** (68%) which, upon treatment with stronger acid, gave **11** (54%). The assigned structures were in full agreement with spectroscopic (^{1}H NMR, IR) and analytical data (see the Experimental Section and supplementary material). The oxidation appears reasonably general, since the presence of bulky 2′-substituents—which would further disrupt the coplanarity of the rings and introduce steric hindrance for the addition of the methyl alcohol residue—did not adversely affect product yields.

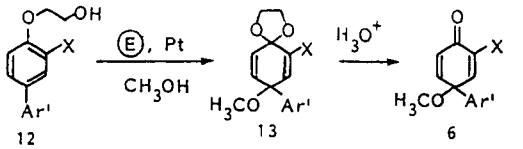


9 10 11

Acid hydrolysis of the *p*-quinol ether dimethyl ketals **5a–c** gave the corresponding *p*-quinol ethers **6a–c** in excellent yields and without formation of any dienone–phenol rearrangement products. However, hydrolysis of *p*-quinol ether ketals **5g,h**, which possess a masked internal nucleophilic group at the 2′-position, afforded the corresponding tricyclic products **7** (53%) and **8** (70%). These products were formed by ketal hydrolysis and deprotection, followed by intramolecular Michael addition of the alcohol and aldehyde hydrate, respectively, to the enone linkage of the *p*-quinol ether. The structural assignment of **8** was supported by ^{1}H NMR homonuclear decoupling experiments and COSY 45 2D-NMR analysis, which confirmed the existence of a long-range coupling between the methine proton and the β-proton of the α,β-unsaturated ketone (see the supplementary material).

Anodic formation of cyclic ketals from aromatic ether linkages containing a nucleophilic center could impart selectively in the oxidation of unsymmetrical biphenyls. Thus, anodic oxidations of biphenyls containing the 2-hydroxyethyl ether side chain were examined. The required biphenyl 2-hydroxyethyl ethers **12a–f** were prepared by reaction of the *p*-arylphenols with ethylene carbonate and tetraethylammonium bromide in dimethylformamide at 140 °C.[11] The biphenyls **12a–f** were anodically oxidized as above to afford the corresponding *p*-quinol ether ethylene glycol ketals **13a–c,e** in excellent yields (Table III). One advantage associated with the use of a 2-hydroxyethyl ether over a simple methyl ether was the increased current efficiency observed in the anodic oxidations of biphenyls 2-hydroxyethyl ethers (ca. 40%) versus the current efficiency observed in the anodic oxidations of biphenyl methyl ethers (ca. 10%). Even more interesting was the result from anodic oxidation of **12c**. Since both rings of **12c** are monooxygenated, the ease of their oxidation should be comparable.[12] However, in the actual oxidation, the *p*-quinol ether ketal arising from selective oxidation of the ring with the 2-hydroxyethyl ether substituent was formed. Unfortunately, the same selectivity was not found in the oxidation of **12d**, since a mixture of products resulted. Thus, it appears that the directing effect of the 2-hydroxyethyl ether substituent is restricted to systems wherein the oxidation potentials of the two aryl rings are similar. One particular limitation of the 1,4-anodic oxidation reaction was observed for compounds having adjacent ether functions such as **12f**. Oxidation of **12f** gave the 1,2-oxidation product, the *o*-quinone diketal **14**, as the only characterized product.[13]

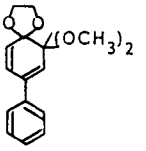
Table III. Anodic Oxidations of 2-Hydroxyethyl Derivatives of Biphenyls



12 13 6

	Ar′	X	% yield 13	% yield 6
a	C_6H_5	H	85	81
b	*o*-$CH_3C_6H_4$	H	84	77
c	*p*-$CH_3OC_6H_4$	H	91[a]	75
d	3,4-$(CH_3OC_6H_3)_2$	H	*b*	
e	2-thiopheneyl	H	79	
f	C_6H_5	OCH_3	*c*	

[a] Controlled potential (0.7–1.3 V versus Pt). [b] Complex mixture. [c] This product was the 1,2-oxidation product (46%).

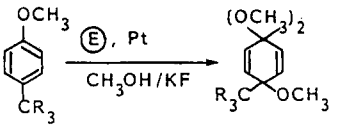


14

Even though the *p*-quinol ether ethylene glycol ketals **13a–c** were more stable toward acid hydrolysis, they were also converted to the respective *p*-quinol ethers **6a–c** in good yield with no evidence of competing dienone–phenol rearrangement.

Anodic Oxidation of *p*-Alkyl-Substituted Aromatic Ethers

Anodic oxidation of 4-methoxybiphenyls offers a direct and often uncomplicated approach to substituted *p*-quinol systems; however, this is typically not the case in the analogous anodic oxidations of *p*-alkyl-substituted aromatic methyl ethers. Although the anodic oxidation of *p*-methylanisole (**15a**) has been rigorously studied under a variety of electrolysis conditions,[4a,7] its oxidation was reexamined under conditions similar to those employed in the biphenyl anodic oxidation work. Thus, the anodic oxidation of *p*-methylanisole was performed in a single-cell apparatus with 1% methanolic potassium fluoride as the solvent/electrolyte using a platinum anode at a constant



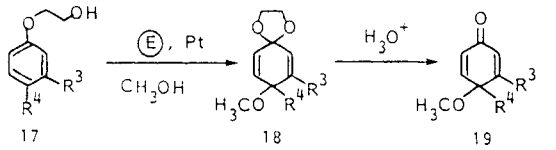
15a, R = H; b, R = D 16a, R = H; b, R = D

(11) (a) Dolson, M. G.; Swenton, J. S. *J. Org. Chem.* **1981**, *46*, 177. (b) Margaretha, P.; Tissot, P. *Helv. Chim. Acta* **1975**, *58*, 933. (c) Reference 4b.

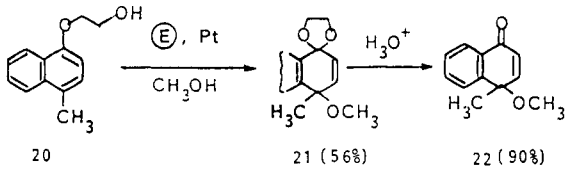
(12) Meites, L.; Zuman, P.; Rupp, P.; Fenner, T.; Narayanan, A. *CRC Handbook Series in Organic Electrochemistry*; CRC: Boca Raton, FL, 1981; Vol. I, p 626.

(13) This process is analogous to that observed in the anodic oxidation studies of catechol ethers. See: (a) Reference 1. (b) Fraser, R. R.; Reyes-Zamora, C. *Can. J. Chem.* **1967**, *45*, 929. (c) Engelhard, M.; Luttke, W. *Chem. Ber.* **1977**, *110*, 3759.

Table IV. *p*-Quinol Ether Ketals and *p*-Quinol Ethers via Anodic Oxidation



	R^3	R^4	% yield 18	% current efficiency	% yield 19
a	H	CH_3	79	28	96
b	H	Et	69	24	91
c	H	*i*-Pr	74	29	89
d	H	*t*-Bu	74	25	*a*
e	CH_3	CH_3	66	26	89
f	H	CH_2Ph	*b*		



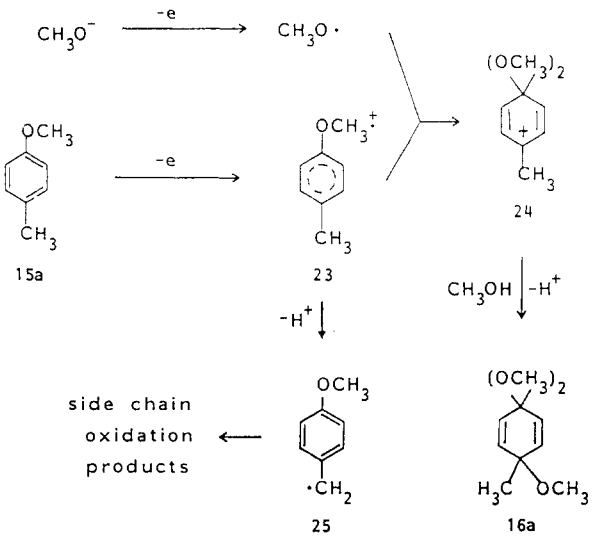
[a] Hydrolysis product is 2-(4-methoxyphenoxy)ethanol (89%). [b] Complex mixture of products.

current of 1.0 A. Quantitative GLC analysis of the anodic oxidation mixture at complete conversion of **15a** indicated that the *p*-quinol ether ketal **16a** was formed in only 8% yield, and at least three other products were also detected. Anodic oxidation of *p*-(trideuteriomethyl)anisole **15b** conducted under the same electrolysis conditions gave the corresponding *p*-quinol ether ketal **16b** in a 19% yield.

The results derived from anodic oxidation of the 2-(4-alkylphenoxy)ethanol derivatives **17a–e** and **20** are in marked contrast to those obtained with *p*-methylanisole. Anodic oxidation of **17a**, in 1% methanolic potassium hydroxide as solvent/electrolyte at a constant current of 1.0 A using a platinum anode, gave **18a** in an 81% yield, but with a low current efficiency (ca. 7%). However, when the same reaction was performed using 1% methanolic potassium fluoride as solvent/electrolyte,[14] **18a** was formed in a 79% yield with a current efficiency of 28%. Since the oxidations proceeded with a ca. fourfold increase in current efficiency in methanolic potassium fluoride versus methanolic potassium hydroxide, all subsequent oxidations were conducted in the former solvent/electrolyte system. Results of the anodic oxidations of **17a–f** and **20** and the hydrolyses of the resulting *p*-quinol ether ketals are reported in Table IV. In all cases except the *p*-benzyl compound **17f**, good yields of nuclear oxidation products resulted. In general, small amounts of competing side-chain oxidation products may be formed—however, they were not isolated—while the desired *p*-quinol ether ketals were obtained pure by a simple chromatographic separation.

The effect of changing the amount of current supplied to the oxidation was also briefly examined. Anodic oxidation of **17a** on a 1-g scale at constant currents of 0.1, 1.0, and 3.25 A afforded **18a** in yields of 85, 79, and 75%, respectively. Although the yield does decrease slightly at higher current, a higher yield is counterbalanced by a substantial increase in reaction time at lower current. Thus, the anodic oxidations in Table IV were conducted at a constant current of 1.0 A.

Scheme II. Mechanistic Sequence for Nuclear and Side-Chain Oxidation



Discussion

The anodic oxidation/acid hydrolysis chemistry of the *p*-arylanisole ethers presented in Tables II and III affords useful synthetic intermediates for the preparation of functionalized and unsymmetrical biphenyl derivatives. Furthermore, this sequence complements the route to *p*-quinol derivatives given in Table I.

The influence of the 2-hydroxyethyl ether side chain on the ratio of nuclear to side-chain oxidation of *p*-alkyl aromatic ethers merits a brief discussion. The anodic oxidation of aromatic ethers in methanol leading to nuclear addition products is thought to proceed via the EEC_rC_p mechanism,[4] as outlined for *p*-methylanisole (Scheme II). The key aspects of this mechanistic sequence are one-electron oxidation of both the aromatic substrate and methoxide ion, followed by radical combination on the surface of the electrode, and finally, reaction of the resulting cation intermediate with methanol. The addition of methoxy radical to the aromatic carbon bearing the ether substituent may be due to the thermodynamic advantage associated with two oxygens attached to an sp^3 carbon.[4b] If methoxide ion is not present, or if the oxidation of methoxide ion is inhibited on the electrode surface by preferential adsorption of the aromatic substrate,[4a] as when carbon anodes are used, then the nuclear addition reaction is slowed.

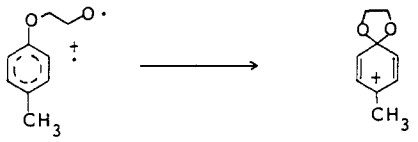
Side-chain oxidation of alkyl-substituted aromatic ethers has been extensively studied;[4,7] it serves as a method for conversion of para-substituted toluenes to acetals of aromatic aldehydes[8] and for the deprotection of benzyl ethers.[15] The crucial step in the mechanism of side-chain oxidation is the loss of a proton from the benzylic carbon to afford a benzyl radical, which is subsequently converted to the benzylic ether. Apparently, further oxidation of the benzylic ether is facile, since most synthetic procedures lead to production of the acetal of the aromatic carbonyl compound.

If the above mechanistic rationales are correct, then any discussion of nuclear versus side-chain oxidation processes

(14) Methanolic potassium fluoride has not been generally employed as a solvent/electrolyte system in the anodic oxidations of aromatic compounds. It was employed without comment in ref 3 and 8. A reviewer has suggested that the lower efficiency in methanolic potassium hydroxide results from oxidation of hydroxide ion to oxygen. Replacement of this hydroxide ion by the more difficultly oxidized fluoride ion then results in an increased current efficiency.

(15) (a) Weinreb, S. M.; Epling, G. A.; Comi, R.; Reitano, M. *J. Org. Chem.* **1975**, *40*, 1356. (b) Garwood, R. F.; Din, N.; Weedon, B. C. L. *J. Chem. Soc., Perkin Trans. 1* **1975**, 2471.

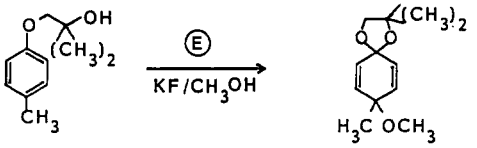
should focus on the relative rates of **23** → **24** and **23** → **25**. The isotope effect observed upon analysis of the ratio of nuclear to side-chain products from the anodic oxidations of **15a** and **15b** supports this assumption. In our work, it has also been demonstrated that the 2-hydroxyethyl side chain markedly favors the nuclear oxidation process. A reasonable interpretation of this observation is that the 2-hydroxyethyl ether side chain provides an intramolecular variant (**26** → **27**) of the reaction of **23** and methoxy radical. This effectively increases the concentration of the



26 **27**

alkoxy radical and favors the formation of the nuclear oxidation product: the *p*-quinol ether ketal. It is known that anodic oxidation of *p*-methylanisole in methanolic sodium methoxide leads to a good yield of **16a**,[4a] presumably because of an increased concentration of methoxy radical, which can then react with **23**.

To further examine how the rate of intramolecular ring closure could promote nuclear versus side-chain oxidation, **28** was prepared, and its anodic oxidation was studied. If the rate of intramolecular ring closure could be accelerated by the *gem*-dialkyl effect,[16] then an even higher yield of quinol ether ketal should be observed. Indeed, anodic oxidation of **28** gave **29** in an 89% yield relative to the 79% yield reported for the oxidation of **17a** → **18a**.



28 **29**

The ca. 400% increase in current efficiency observed when methanolic potassium fluoride was substituted for methanolic potassium hydroxide in the anodic oxidations is an important experimental observation. A discussion of this effect would be premature; however, it is important to note that the use of methanolic potassium fluoride as the solvent/electrolyte in the oxidation of *p*-methoxyanisole (**15a**) did not have a dramatic effect on the ratio of nuclear versus side-chain oxidation products.

Summary

The anodic oxidation of *p*-aryl and *p*-alkyl aromatic ethers possessing a 2-hydroxyethyl side chain affords the corresponding *p*-quinol ether ketals in 66–82% yields. While simple *p*-alkyl groups do not markedly affect the yield of nuclear oxidation products, anodic oxidation of **17f** affords a mixture of products due to facile side-chain oxidation of the *p*-benzyl substituent. The use of methanolic potassium fluoride as the solvent/electrolyte results in an increased efficiency for the reaction. Since these oxidations can be performed at a constant current (1.0–2.0 A) in a single cell, preparative-scale reactions can readily be conducted with equipment available in most chemical laboratories by workers with minimal electrochemical experience. These electrochemically derived *p*-quinol ether ketals can usually be hydrolyzed in good yield to the corresponding quinol ethers, which offer a number of options for further synthetic transformations.

Experimental[17] Section

Reaction of Quinone Monoketals with Aryllithium Reagents. The procedure for **2a** is representative of the addition of aryllithium reagents to quinone monoketals. For the subsequent compounds, only the yields (see Table I), purification procedure, and spectroscopic data are given.

2a. To a solution of 1[2b,18] (0.5 g, 3.2 mmol) in THF (5.0 mL) at −78 °C was added a 1.6 M aliquot of phenyllithium (2.1 mL, 3.36 mmol) over a 5-min period. The reaction was monitored by TLC (3:1 Et_2O/PE as eluant) and judged to be complete after 30 min. The reaction mixture was poured into a brine solution (10 mL), and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic layers were dried ($CaSO_4$) and concentrated in vacuo to yield a yellow oil (0.732 g, 98%). The crude product (0.732 g, 3.0 mmol) was dissolved in $(CH_3)_2CO$ (10 mL), and an 8% HOAc solution (10 mL) was added. The hydrolysis mixture was stirred at 25 °C for 2.0 h, during which time the mixture turned light yellow. After 2.0 h, the reaction was judged to be complete by TLC (3:2 Et_2O/PE as eluant). The $(CH_3)_2CO$ was removed at reduced pressure, and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried ($CaSO_4$) and concentrated in vacuo to yield an oily solid, which was recrystallized from THF to afford **2a** (0.422 g, 78%) as white needles: mp 99–100 °C; IR (KBr) 3423 (s), 1662 (s), 1611 (s), 1449 (m), 1397 (m), 1388 (m), 1369 (m), 1160 (s), 1065 (m), 1052 (m), 993 (s), 860 (s), 753 (s), 700 (s); ^1H NMR δ 7.42–7.23 (m, 5 H), 6.54 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 55 Hz, 4 H), 2.66 (s, disappears upon D_2O wash, 1 H); mass spectrum, exact mass calcd for $C_{12}H_{10}O_2$ *m/e* 186.0681, obsd 186.0725.

2b. Reaction of the lithium compound derived from *o*-bromotoluene with 1 as described for **2a** gave a yellow solid, which was recrystallized from Et_2O to yield **2b** (76%) as a white solid: mp 112–114 °C; IR (KBr) 3403 (s), 1660 (s), 1620 (s), 1480 (m), 1391 (m), 1381 (m), 1356 (m), 1161 (m), 1058 (m), 1023 (m), 949 (s), 859 (s), 758 (s); ^1H NMR δ 7.76–7.58 (m, 1 H), 7.32–7.14 (m, 3 H), 6.59 (AB q, J_{AB} = 8 Hz, $\Delta\nu$ = 52 Hz, 4 H), 2.33 (s, 3 H), 2.23 (s, disappears upon D_2O wash, 1 H); mass spectrum, exact mass calcd for $C_{13}H_{12}O_2$ *m/e* 200.0836, obsd 200.0836.

2c. Reaction of the lithium compound derived from *p*-bromoanisole with 1 as described for **2a** gave a yellow solid, which was recrystallized from EtOAc/Et_2O to yield **2c** (79%): mp 124.5–126 °C; IR (KBr) 3430 (s), 1660 (s), 1621 (s), 1609 (s), 1599 (m), 1508 (s), 1469 (m), 1441 (m), 1393 (m), 1382 (m), 1362 (m), 1302 (m), 1254 (s), 1190 (m), 1180 (m), 1171 (s), 1161 (s), 1062 (m), 1052 (s), 1023 (s), 948 (s), 912 (m), 858 (s), 829 (s); ^1H NMR δ 7.36 (left wing of an AB q, J_{AB} = 9 Hz, 2 H), 6.86 (2 br s due to overlapping wings of AB q, J_{AB} = 9 Hz, 4 H), 6.14 (right wing of an AB q, J_{AB} = 10 Hz, 2 H), 3.77 (s, 3 H), 2.90 (s, disappears

(16) Hine, *J. Structural Effects on Equilibria in Organic Chemistry*; Wiley: New York, 1975; pp 284–295.

(17) All melting points were determined in capillaries in a Thomas-Hoover Unimelt capillary melting point apparatus and are uncorrected. Reported boiling points are also uncorrected. Infrared spectra were determined on a Perkin-Elmer Model 283B spectrometer as KBr disks unless otherwise noted, reported in reciprocal centimeters, and calibrated with the polystyrene band at 1601.4 cm^{-1}. ^1H NMR spectra were determined at 80 MHz on an IBM NR 80 spectrometer with deuteriochloroform as solvent and residual chloroform as standard. The ^{13}C NMR spectra were recorded at 20 MHz on an IBM NR 80 instrument. Mass spectral and exact mass measurements were obtained by Richard Weisenberger on a Kratos MS-30 mass spectrometer. Column chromatography of quinol ether ketals was carried out with neutral alumina (activity III) unless otherwise stated. Alumina and silica gel were obtained from E. Merck Co. Tetrahydrofuran (THF) was purified by distillation from benzophenone ketyl directly into the reaction flask. Dimethylformamide (DMF) was freshly distilled from barium oxide before use. Methyllithium in diethyl ether, *sec*-butyllithium in cyclohexane, *n*-butyllithium in hexanes, and phenyllithium in cyclohexane were used fresh and obtained from Aldrich Chemical Co. Petroleum ether, bp 35–60 °C (PE), diethyl ether (Et_2O), ethyl acetate (EtOAc), benzene (C_6H_6), chloroform ($CHCl_3$), and all other solvents used in chromatography were dried and distilled before use. Standard workup refers to extraction with $CHCl_3$, CH_2Cl_2, or Et_2O, drying over Na_2SO_4 or $CaSO_4$, concentration, and drying in vacuo.

(18) The 4,4-dimethoxy-2,5-cyclohexadien-1-one (1) is commercially available (Aldrich) but can be readily prepared via the anodic oxidation/hydrolysis route discussed in ref 2b and 2c.

upon D_2O wash, 1 H); mass spectrum, exact mass calcd for $C_{13}H_{12}O_3$ m/e 216.0866, obsd 216.0801.

Direct Formation of 3d. To a solution of 4-iodo-1,2-dimethoxybenzene (0.5 g, 1.8 mmol) in THF (5.0 mL) at −78 °C was added a 1.5 M aliquot of *n*-BuLi (1.5 mL, 2.3 mmol) over a 5-min period, during which time the homogeneous solution turned to a milky yellow suspension. To this solution was added 1 (0.28 g, 1.8 mmol) as a solution in THF (5.0 mL). Workup as described for **2a** gave the crude addition product, which was dissolved in THF (20.0 mL) to which Zn/Cu couple (1.0 g, 15.0 mmol) was added, and the reaction mixture was heated to reflux. Next, 20% HOAc (5.0 mL) was added, and the reaction mixture was then heated at reflux for an additional 6.0 h. Standard workup gave a tan solid, which was recrystallized from $CHCl_3$ to afford the phenol **3d** (0.207 g, 50% overall from 1): mp 153–155 °C; IR (KBr) 3435 (s), 1616 (m), 1599 (m), 1508 (s), 1472 (m), 1452 (s), 1440 (m), 1278 (m), 1270 (s), 1248 (s), 1220 (s), 1170 (s), 1140 (s), 1021 (s), 831 (m), 810 (m), 769 (m); ^1H NMR δ 7.43 (left wing of an AB q, J_{AB} = 9 Hz, 2 H), 7.2–6.7 (str m, 5 H), 4.7 (br s, 1 H), 3.92 (s, 3 H), 3.89 (s, 3 H); mass spectrum, exact mass calcd for $C_{14}H_{14}O_3$ m/e 230.0943, obsd 230.0929.

Reaction of 2-Lithiothiophene with 1. To a solution of thiophene (1.0 g, 12 mmol) in dry THF (10.0 mL) at −78 °C was added a 1.6 M aliquot of *n*-BuLi (7.8 mL, 12.5 mmol). The solution was stirred for 20 min at −78 °C, during which time the reaction mixture turned milky white, and then 1 (1.8 g, 12.0 mmol) was added as a solution in dry THF (10.0 mL). Workup as before gave a white solid, which was recrystallized from Et_2O to give the quinol ether ketal (59%): mp 79–81 °C; IR (KBr) 3420 (s, br), 3100 (m), 3080 (m), 2998 (m), 2970 (m), 2946 (m), 2830 (m), 1440 (m), 1410 (s), 1357 (m), 1338 (m), 1311 (m), 1239 (m), 1212 (m), 1181 (m), 1150 (s), 1100 (s), 1077 (m), 1037 (s), 1020 (s), 998 (m), 989 (m), 942 (s), 915 (s), 890 (s), 845 (m), 702 (s); ^1H NMR δ 7.27–7.19 (m, 1 H), 6.96–6.89 (two-line m, 2 H), 6.11 (AB q, J_{AB} = 11 Hz, $\Delta\nu$ = 25 Hz, 4 H), 3.33 (s, 3 H), 3.28 (s, 3 H), 2.4 (br s, disappears upon D_2O wash, 1 H); mass spectrum, exact mass calcd for $C_{12}H_{14}O_3S$ m/e 238.0663, obsd 238.0676.

2f. Reaction of phenyllithium with 3,4,4-trimethoxy-2,5-cyclohexadien-1-one[2b] as described for **2a** gave a light yellow solid, which was recrystallized from CH_2Cl_2/Et_2O to afford **2f** (70%): mp 167–168 °C with some decomposition; IR (KBr) 3475 (s), 3070 (m), 3008 (m), 2985 (m), 2845 (m), 1669 (s), 1645 (s), 1612 (s), 1592 (m), 1450 (s), 1428 (m), 1395 (m), 1370 (s), 1240 (m), 1210 (s), 1172 (s), 1161 (s), 1103 (s), 1038 (s), 995 (s), 936 (s), 880 (s), 855 (m), 837 (s), 755 (s), 695 (s); ^1H NMR δ 7.51–7.24 (m, 5 H), 6.52 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 48 Hz, left wing meta-coupled, J_{AB} = 3 Hz, 2 H), 5.82 (d, J = 3 Hz, 1 H), 3.64 (s, 3 H), 2.57 (s, 1 H); mass spectrum, exact mass calcd for $C_{13}H_{12}O_3$ m/e 216.0780, obsd 216.0788.

Reduction of *p*-Arylquinols to *p*-Arylphenols. The following procedure used for the preparation of **3b** is representative of the synthetic method employed in subsequent systems, for which only the purification procedure and spectroscopic data have been given. The zinc/copper couple was freshly prepared.[19]

3b. To a suspension of the *p*-quinol **2b** (1.8 g, 9.0 mmol) and Zn/Cu couple (1.0 g, 18.0 mmol) in THF (10.0 mL) at reflux was added 20% HOAc (10.0 mL). After 6.0 h of heating at reflux, the reaction was judged to be complete by TLC (2:1 PE/Et_2O as eluant) and the mixture poured into a cold 10% HCl solution (30.0 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL), the combined organic layers were dried (Na_2SO_4), and concentration in vacuo gave a white solid. Low-temperature recrystallization from Et_2O/PE afforded **3b** (1.1 g, 66%) as a white solid: mp 66–68 °C (lit.[20] mp 84–85 °C); IR (KBr) 3400 (s, br), 1611 (m), 1599 (m), 1515 (s), 1481 (s), 1440 (m, br), 1378 (m), 1238 (s), 831 (s), 757 (s); ^1H NMR δ 7.43 (br left wing of an AB q, J_{AB} = 9 Hz, 2 H), 7.20–7.13 (m, 4 H), 6.85 (right wing of an AB q, J_{AB} = 9 Hz, 2 H), 4.86 (s, disappears upon D_2O wash, 1 H), 2.36 (s, 3 H); mass spectrum, exact mass calcd for $C_{13}H_{12}O$ m/e 184.0888, obsd 184.0902.

3a. Recrystallization from CH_3OH/CCl_4 gave **3a** as a white solid, mp 155–156 °C (lit.[21] mp 165–167 °C).

3c. Recrystallization from EtOAc gave **3c** as a white solid: mp 172–174 °C; IR (KBr) 3420 (s, br), 1609 (m), 1599 (m), 1499 (s), 1245 (s), 1178 (s), 1037 (s), 813 (s); ^1H NMR δ 7.52–7.34 (m, 4 H), 7.00–6.82 (m, 4 H), 4.67 (s, 1 H), 3.84 (s, 3 H); mass spectrum, exact mass calcd for $C_{13}H_{12}O_2$ m/e 200.0838, obsd 200.0827.

3e. Recrystallization from Et_2O/PE gave **3e** as a white solid: mp 135–137.5 °C; IR (KBr) 3430 (s, br), 1615 (m), 1538 (m), 1506 (s), 1450 (m), 1432 (m), 1378 (m), 1262 (sh), 1260 (s), 1182 (m), 1110 (m), 852 (m), 827 (m), 819 (s), 702 (m), 688 (s); ^1H NMR δ 7.46–6.99 (m, 3 H), 7.21 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 55 Hz, 4 H), 5.09 (br s, 1 H); mass spectrum, exact mass calcd for $C_{10}H_8OS$ m/e 176.0296, obsd 176.0307.

3f. Flash chromatography on silica gel (C_6H_6 as eluant) gave **3f** as a white solid: mp 63–66 °C (sample recrystallized from C_6H_6, mp 66–67 °C); IR (KBr) 3520 (s), 1615 (sh), 1608 (m), 1535 (m), 1495 (sh), 1490 (s), 1451 (s), 1420 (m), 1309 (s), 1258 (s), 1205 (s), 1199 (sh), 1127 (m), 1021 (m), 1017 (m), 854 (m), 819 (m), 790 (m), 770 (sh), 759 (s), 700 (s); ^1H NMR δ 7.50–7.01 (m, 8 H), 5.61 (s, 1 H), 3.94 (s, 3 H); mass spectrum, exact mass calcd for $C_{13}H_{12}O_2$ m/e 200.0837, obsd 200.0829.

Electrolysis of 4-Arylanisoles and 2-Hydroxyethyl Ethers of 4-Arylphenols. All anodic oxidations were conducted with a Kepco Model JQE 36-3M power supply in a single cell at constant current, employing a platinum gauze anode (typical size: 33-mm diameter × 28-mm height) surrounding a platinum sheet cathode (12 mm × 25 mm) with 1% methanolic potassium hydroxide as the solvent/supporting electrolyte system unless otherwise noted. The voltage of the power supply was not critical to the reactions and varied from 5 to 12 V, depending on the current. The electrolysis of **4c** is representative of the procedure employed in subsequent anodic oxidations for which the following information is given: grams (moles) anodically oxidized; volume of 1% methanolic potassium hydroxide; constant current employed, elapsed time of oxidation, temperature; the purification procedure and spectroscopic properties of the products.

4c. The 4,4′-dimethoxybiphenyl[22] (**4c**; 9.1 g, 42.5 mmol) was suspended in the standard solvent/electrolyte system (500 mL), and this slurry was electrolyzed at a constant current of 2.0 A for a total of 8.0 h at 20 °C. After 6.0 h, the electrolysis mixture became homogeneous. After 8.0 h, TLC (35% Et_2O/PE) indicated there was no remaining starting material. The CH_3OH was removed at reduced pressure, and the residue was diluted with distilled water (50 mL) and extracted with $CHCl_3$ (3 × 50 mL). The organic layers were combined and dried ($CaSO_4$), and the solvent was removed in vacuo to yield **5c** (11.3 g, 96%) as a yellow-brown oil suitable for future use. A 3.0-g electrolysis conducted similarly was purified by molecular distillation [bath temperature 100 °C (0.3 mm)] to afford **5c** (2.82 g, 76%) as a light yellow oil: IR (neat) 2930 (s), 2900 (s), 2820 (s), 1610 (m), 1510 (s), 1461 (m), 1400 (m), 1301 (m), 1250 (s), 1170 (s), 1100 (s), 1060 (s), 1035 (s), 950 (s), 830 (m); ^1H NMR δ 7.09 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 43 Hz, 4 H), 6.04 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 19 Hz, 4 H), 3.76 (s, 3 H), 3.56 (s, 3 H), 3.33 (s, 3 H), 3.29 (s, 3 H); mass spectrum, exact mass calcd for $C_{16}H_{20}O_4$ m/e 276.1362, obsd 276.1334.

4a: 0.1 g (0.54 mmol); 70.0 mL; 1.0 A for 0.25 h at 20 °C. Flash column chromatography (C_6H_6 as eluant) yielded a water white oil (0.82 g, 74%): IR (neat) 3040 (m), 2990 (sh), 2942 (s), 2910 (sh), 2830 (s), 1491 (m), 1465 (m), 1450 (s), 1400 (s), 1210 (m), 1200 (m), 1175 (m), 1105 (sh), 1070 (s), 1038 (m), 865 (s, br), 910 (s), 752 (s), 730 (s), 699 (s); ^1H NMR δ 7.54–7.26 (m, 4 H), 6.08 (AB, q, J_{AB} = 10 Hz, $\Delta\nu$ = 21 Hz, 4 H), 3.39 (s, 3 H), 3.36 (s, 3 H), 3.33 (s, 3 H); mass spectrum, exact mass calcd for $C_{15}H_{18}O_3$ m/e 246.1256, obsd 246.1250.

4b: 0.14 g (0.7 mmol); 70.0 mL; 1.0 A for 0.75 h at 20 °C. Flash column chromatography (C_6H_6 as eluant) afforded a clear oil (0.116 g, 64%): IR (neat) 2939 (s), 2823 (m), 1460 (m), 1451 (m), 1401 (m), 1200 (m), 1172 (m), 1100 (s), 1080 (s), 1070 (s), 1035 (s), 902 (m), 817 (m); ^1H NMR δ 7.67–7.31 (m, 1 H), 7.23–7.10 (m, 3 H), 6.11 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 20 Hz, 4 H), 3.37 (s, 3 H), 3.29 (s, 3 H), 3.24 (s, 3 H), 2.43 (s, 3 H); mass spectrum, exact mass calcd for $C_{16}H_{20}O_3$ m/e 260.1413, obsd 260.1436.

(19) Blankenship, R. M.; Burdett, K. A.; Swenton, J. S. *J. Org. Chem.* **1974**, *39*, 2300.
(20) Kliegel, A.; Huber, H. *Ber. Dtsch. Chem. Ges.* **1920**, *53*, 1646.
(21) *Aldrich Catalog/Handbook of Fine Chemicals*, 1986–1987; Aldrich: Milwaukee, 1986; p 1075.
(22) Fanta, P. E. *Synthesis* **1974**, 9.

4g → 5g → 7: 0.22 g (0.67 mmol); 70.0 mL; 0.5 A for 0.75 h at 10 °C. Flash column chromatography (2:1 C_6H_6/PE as eluant) afforded **5g** as a clear oil (226 mg, 86%). This material could not be obtained analytically pure and was used immediately in the next step. The quinol ether ketal had the following spectroscopic data: IR (neat) 2960 (s), 2940 (s), 2905 (s), 2865 (s), 2838 (m), 1475 (s), 1468 (s), 1455 (sh), 1408 (m), 1258 (s), 1201 (s), 1155 (m), 1110 (s), 1075 (s, br), 1045 (s, br), 980 (m), 960 (s), 940 (m), 837 (s), 778 (s), 758 (s); ^{1}H NMR δ 7.74–7.24 (m, 4 H), 6.09 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 20 Hz, 4 H), 4.94 (s, 2 H), 3.37 (s, 3 H), 3.31 (s, 3 H), 3.23 (s, 3 H), 0.95 (s, 9 H), 0.10 (s, 6 H).

The crude ketal prior to chromatography was dissolved in an acetone/water (1:1) solution (20.0 mL) and cooled to 0 °C, and then a 10% HCl solution (0.1 mL) was added. This mixture was stored for 3.0 h at −8 °C before a saturated $NaHCO_3$ solution (10.0 mL) was added to quench the hydrolysis. Workup as usual afforded a yellow oil. Chromatography on silica gel ($CHCl_3$ as eluant) gave **7** (0.1 g, 53% overall from **4g**) as white needles: mp 81–83 °C; IR (KBr) 2970 (m), 2960 (m), 2910 (m), 2851 (m), 2840 (m), 1680 (s), 1660 (sh), 1450 (m), 1389 (m), 1371 (m), 1281 (m), 1219 (m), 1117 (m), 1090 (s), 1078 (s), 1039 (m), 1021 (m), 990 (m), 968 (m), 771 (m), 760 (m); ^{1}H NMR δ 7.6–6.96 (m, 4 H), 6.33 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 57 Hz, lower field component split, J_{AB} = 2 Hz, 2 H), 4.81 (s, 2 H), 4.50–4.38 (m, 1 H), 3.18 (s, 3 H), 2.94 (low-field portion of AB of ABX partly obscured by the methoxy peak), 2.67 (right wing of an ABX, J_{AB} = 16 Hz, J_{AX} = 4 Hz, $\Delta\nu$ = 29 Hz, 1 H); mass spectrum, exact mass calcd for $C_{14}H_{14}O_3$ m/e 230.0943, obsd 230.0949.

4h → 5h → 8: 0.117 g (0.45 mmol); 70.0 mL; 0.4 A for 1.5 h at 10 °C. Flash column chromatography (1:1 PE/Et_2O as eluant) afforded **5h** (0.106 g, 77%) as a clear oil, which could not be obtained analytically pure: IR (neat) 2940 (s), 2910 (s), 2835 (s), 1464 (m), 1450 (m) 1405 (m), 1380 (m), 1356 (m), 1200 (s, br), 1109 (s, br), 1070 (s, br), 958 (s), 809 (s); ^{1}H NMR δ 7.76–7.68 (m, 1 H), 7.54–7.24 (m, 3 H), 6.09 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 13 Hz, 4 H), 6.04 (s, 1 H), 3.47 (s, 3 H), 3.37 (s, 6 H), 3.31 (s, 3 H), 3.26 (s, 3 H).

The impure electrolysis product **5h** was hydrolyzed in an acetone/10% HCl (1:1) solution (20.0 mL) at 25 °C for 10.0 h and worked up similarly to the **4g → 7** hydrolysis to afford a white solid, which was recrystallized from $CHCl_3$ to give **8** (0.062 g, 70% overall from **4h**): mp 170–172 °C; IR (KBr) 3460 (s, br), 1690 (s), 1069 (s), 1042 (m), 1021 (m), 1009 (m); ^{1}H NMR δ 7.64–7.32 (m, 4 H), 6.29 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 43 Hz, right wing of an AB q overlapping with the tertiary benzylic hydrogen, 2 H, the left wing shows an additional coupling constant of J_{AB} = 3 Hz, 1 H), 5.08 (str, m, 1 H), 3.19 (s, 3 H), 2.85 (ABX, right wing, J = 18 Hz, 3 Hz, $\Delta\nu$ = 36 Hz, the low-field component is partly obscured by the methoxy peak, 2 H); mass spectrum, exact mass calcd for $C_{14}H_{14}O_4$ m/e 246.0892, obsd 246.0901.

4i → 9. 4i (0.2 g, 0.88 mmol) and 1% methanolic potassium hydroxide (50 mL) were placed in the anode compartment of an H-cell. In the cathode compartment was placed 1% methanolic potassium hydroxide (60 mL). The reaction was electrolyzed at a constant current of 0.3 A for 1.0 h at 0 °C. After 1.0 h, the electrolysis mixture was neutralized with CO_2, and the CH_3OH was removed at reduced pressure. The residue was diluted with distilled water (10.0 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo to give a solid, which was recrystallized from Et_2O, affording **9** (0.122 g, 54%) as white needles: mp 109–110 °C; IR (KBr) 1768 (s), 1465 (m), 1403 (m), 1388 (m), 1251 (m), 1216 (m), 1094 (s), 1070 (s), 1022 (m), 978 (m), 939 (s); ^{1}H NMR δ 7.85–7.33 (m, 4 H), 6.03 (AB q, J_{AB} = 8 Hz, $\Delta\nu$ = 29 Hz, 4 H), 3.45 (s, 3 H), 3.33 (s, 3 H). Anal. Calcd for $C_{15}H_{14}O_4$: C, 69.75; H, 5.46. Found: C, 70.21; H, 5.00.

4i → 10. In the anode compartment of an H-cell was placed **4i** (1.1 g, 4.8 mmol) dissolved in 1% methanolic potassium hydroxide (50.0 mL), and in the cathode compartment was placed 1% methanolic potassium hydroxide (50.0 mL). The reaction mixture was electrolyzed at 0.3 A for 3.0 h at 0 °C; the potential was varied to keep the current constant. The reaction was monitored by TLC (EtOAc as eluant) and judged to be complete after 3.0 h. The CH_3OH was removed at reduced pressure, and the residue was diluted with distilled water (150 mL) and $CHCl_3$ (200 mL). This mixture was carefully acidified to pH 6.0, the layers were separated, and the aqueous phase was extracted with $CHCl_3$ (3 × 50 mL). The combined organic layers were dried ($CaSO_4$) and concentrated in vacuo to yield a foam, which was triturated with Et_2O to give a white solid (mp 129–132 °C), which was recrystallized from CH_2Cl_2/PE to afford **10** (0.8 g, 68%) as white needles: mp 131–133 °C; IR (KBr) 3495 (m), 1720 (s), 1650 (s), 1602 (m), 1320 (m), 1260 (m), 1240 (m), 1130 (m), 1105 (m), 1002 (m), 780 (m); ^{1}H NMR δ 8.11–8.02 (m, 1 H), 7.74–7.44 (m, 3 H), 5.99 (br, 2 H), 5.22 (left wing of an AB q, J_{AB} = 6 Hz, 1 H), 4.91 (br d, J_d = 6 Hz, 1 H), 3.63 (s, 3 H), 2.60 (s, disappears upon D_2O wash, 1 H); mass spectrum, exact mass calcd for $C_{14}H_{12}O_4$ m/e 243.9889, obsd 244.0731.

12a: 0.19 g (0.9 mmol); 70.0 mL; 1.0 A for 5 min at 20 °C. Flash column chromatography on silica gel (C_6H_6 as eluant) gave **12a** (0.186 g, 85%) as a light yellow oil: IR (neat) 2930 (m), 2880 (m), 2820 (m), 1498 (m), 1460 (m), 1448 (m), 1405 (m), 1305 (m), 1199 (m, br), 1175 (m), 1111 (s), 1070 (s, br), 1021 (s), 961 (s, br), 750 (m), 695 (m); ^{1}H NMR δ 7.60–7.22 (m, 5 H), 5.98 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 12 Hz, 4 H), 4.11 (s, 4 H), 3.36 (s, 3 H); mass spectrum, exact mass calcd for $C_{15}H_{16}O_3$ m/e 244.1099, obsd 244.1085.

12b: 0.2 g (0.9 mmol); 65.0 mL; 0.5 A for 1.25 h at 10 °C. Flash column chromatography (1:1 C_6H_6/PE as eluant) gave **12b** (0.179 g, 84%) as a colorless oil: IR (neat) 2938 (m), 2890 (m), 1588 (m), 1487 (s), 1458 (m), 1403 (m), 1280 (m), 1240 (s), 1110 (s), 1068 (s, br), 963 (s), 942 (s); ^{1}H NMR δ 7.38–7.04 (m, 4 H), 5.93 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 12 Hz, 4 H), 4.09 (s, 4 H), 3.31 (s, 3 H), 2.29 (s, 3 H); mass spectrum, exact mass calcd for $C_{16}H_{18}O_3$ m/e 258.1255, obsd 258.1244.

12c: 0.2 g (0.8 mmol); 70.0 mL; controlled potential versus platinum, 0.7–1.3 V, 0.2 A for 1.0 h at 10 °C. Flash column chromatography (C_6H_6 as eluant) gave **13c** (0.201 g, 91%) as a yellow oil: IR (KBr) 2938 (m), 2885 (m), 1609 (m), 1511 (s), 1462 (m), 1403 (m), 1301 (m), 1257 (s), 1199 (m), 1171 (s), 1112 (s), 1080 (s), 1035 (s), 999 (m), 967 (s), 948 (s), 831 (m); ^{1}H NMR δ 7.09 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 43 Hz, 4 H), 5.92 (AB q, J_{AB} = 12 Hz, $\Delta\nu$ = 16 Hz, 4 H), 4.08 (s, 4 H), 3.75 (s, 3 H), 3.30 (s, 3 H); mass spectrum, exact mass calcd for $C_{16}H_{18}O_4$ m/e 274.1205, obsd 274.1197.

12e: 0.2 g (1.0 mmol); 70.0 mL; 0.2 A for 0.58 h at 10 °C. Flash column chromatography (C_6H_6 as eluant) gave **13e** (0.198 g, 79%) as a very light yellow oil: IR (neat) 2990 (m), 2941 (m), 2897 (m), 2839 (m), 1469 (m), 1440 (m), 1410 (s), 1391 (m), 1233 (m), 1199 (s), 1170 (m), 1117 (s), 1075 (s, br), 1021 (s), 969 (s), 949 (s), 919 (m), 850 (m), 832 (m), 730 (m), 703 (m), 685 (m); ^{1}H NMR δ 7.20–7.16 (m, 1 H), 6.92–6.88 three-line m, 2 H), 6.01 (s, 4 H), 4.07 (s, 4 H), 3.29 (s, 3 H); mass spectrum, exact mass calcd for $C_{13}H_{14}O_3S$ m/e 250.0664, obsd 250.0662.

12f: 0.2 g (0.8 mmol); 70.0 mL; 0.5 A for 5 min at 20 °C. Flash column chromatography (C_6H_6 as eluant) gave **14** (0.1 g, 46%) as a clear oil: IR (neat) 3055 (m), 3030 (m), 2940 (s), 2893 (m), 2825 (m), 1490 (m), 1479 (m), 1445 (m), 1392 (m), 1310 (m), 1250 (m), 1180 (s), 1149 (s), 1135 (s), 1085 (s), 1060 (s), 1040 (s), 1032 (s), 942 (s), 761 (m), 740 (m), 698 (m), 679 (m); ^{1}H NMR δ 7.47–7.22 (m, 5 H), 6.16 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 30 Hz, overlapping with vinyl hydrogen, left wing coupled to meta hydrogen, J_{AB} = 2 Hz, 3 H), 4.18 (s, 4 H), 3.43 (s, 6 H); mass spectrum, exact mass calcd for $C_{16}H_{18}O_4$ m/e 274.1205, obsd 274.1202.

Anodic Oxidation of 2-(4-Alkylphenoxy)ethanols. The procedure for the anodic oxidation of **17a** is given in detail. Unless otherwise specified, the anodic oxidations were performed in a single-cell, jacketed apparatus, using a circular platinum gauze anode (33-mm diameter × 28-mm height) and a platinum sheet cathode (8 mm × 2 mm) with 1% methanolic potassium fluoride (by weight) acting as both solvent and electrolyte at 10 °C, with a Kepco Model JQE 36-3M power supply. The current was maintained at 1.0 A and the voltage at 10–12 V. Since the oxidations of **17b–e**, **20**, and **28** were performed in a similar manner, only the purification procedure and spectroscopic data for the products are given.

17a. A clear homogeneous solution of **17a** (5.0 g, 32.9 mmol) in the solvent/electrolyte (250 mL) was electrolyzed for 6.3 h, after which time the reaction was judged to be complete by TLC (3:1 PE/Et_2O as eluant). As the reaction progressed, the colorless solution remained homogeneous but turned an amber color. The CH_3OH was removed in vacuo (60 °C, final bath temperature), and the dark yellow brown residue was diluted with water (50

mL). The organic product was extracted with CH_2Cl_2 (3 × 50 mL), washed with brine solution (30 mL), and dried (Na_2SO_4). Removal of the solvent at reduced pressure afforded a golden oil (5.12 g), which was chromatographed (2.5 cm × 25 cm column, 4% Et_2O/PE as eluant) to give **18a** (4.75 g, 79%) as a clear colorless oil: IR (neat) 2983 (m), 2939 (m), 2897 (m), 1409 (s), 1301 (m), 1292 (s), 1140 (s), 1111 (s), 1090 (s), 1053 (s), 1017 (s), 968 (s), 948 (s), 770 (m), 702 (m); ^1H NMR δ 5.86 (s, 4 H), 4.02 (s, 4 H), 3.09 (s, 3 H), 1.28 (s, 3 H); mass spectrum, exact mass calcd for $C_{10}H_{14}O_3$ m/e 182.0943, obsd 182.0911.

17b. Chromatography (1.8 cm × 15 cm column, 8% Et_2O/C_6H_6 as eluant) gave **18b** as a clear colorless oil: IR (neat) 2935 (s), 2920 (s), 1610 (s), 1511 (s), 1480 (s), 1461 (s), 1440 (m), 1369 (m), 1294 (m), 1260 (s), 1245 (s), 1198 (m), 1180 (s), 1117 (m), 1090 (s), 1071 (s), 1050 (s), 970 (s), 830 (m), 760 (m); ^1H NMR δ 5.85 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 20 Hz, 4 H), 4.03 (s, 4 H), 3.12 (s, 3 H), 1.60 (q, J = 7 Hz, 2 H), 0.78 (t, J = 7 Hz, 3 H); mass spectrum, exact mass calcd for $C_{11}H_{16}O_3$ m/e 196.1099, obsd 196.1052.

17c. Chromatography (1.8 cm × 15 cm column, 6% EtOAc/PE as eluant) gave **18c** as a clear colorless oil: IR (neat) 2985 (s), 2937 (s), 2830 (s), 1635 (s), 1510 (s), 1450 (s), 1395 (s), 1303 (s), 1245 (m), 1212 (m), 1170 (m), 1090 (s, br), 1050 (m), 860 (s); ^1H NMR δ 5.86 (AB q, J_{AB} = 10.5 Hz, $\Delta\nu$ = 20.5 Hz, 4 H), 4.02 (s, 4 H), 3.09 (s, 3 H), 1.81 (septet, J = 8 Hz, 1 H), 0.85 (d, J = 7 Hz, 6 H); mass spectrum, exact mass calcd for $C_{12}H_{18}O_3$ m/e 210.1256, obsd 210.1228.

17d. Chromatography (1.8 cm × 15 cm column, 7% EtOAc/C_6H_6 as eluant) gave **18d** as a clear colorless oil: IR (neat) 2959 (m), 2880 (m), 1405 (m), 1361 (m), 1112 (s), 1075 (s), 1019 (m), 1001 (m), 957 (s), 945 (m); ^1H NMR δ 5.95 (s, 4 H), 4.03 (s, 4 H), 3.07 (s, 3 H), 0.91 (s, 9 H); mass spectrum, exact mass calcd for $C_{13}H_{20}O_3$ m/e 224.1412, obsd 224.1358.

17e. Chromatography (2.5 cm × 25 cm column, 5% Et_2O/C_6H_6 as eluant) gave **18e** as a colorless oil: IR (neat) 2987 (m), 2893 (m), 1401 (s), 1309 (m), 1290 (s), 1141 (s), 1110 (s), 1091 (s), 1057 (s), 1013 (s), 964 (s), 946 (s), 775 (m); ^1H NMR δ 6.10 (m, 2 H), 5.87 (m, 1 H), 4.02 (s, 4 H), 3.12 (s, 3 H), 1.81 (m, 3 H), 1.38 (s, 3 H); mass spectrum, exact mass calcd for $C_{11}H_{16}O_3$ m/e 196.1099, obsd 196.1097.

20. Chromatography (1.8 cm × 20 cm column, 6% EtOAc/PE as eluant) gave **21** as a clear colorless oil: IR (neat) 2960 (s), 2935 (s), 1550 (s, br), 1252 (s), 1150 (m), 1097 (s), 1060 (m), 1005 (s), 970 (s), 862 (s); ^1H NMR δ 7.63–7.26 (m, 4 H), 6.06 (d, J_{AB} = 2.7 Hz, 2 H), 4.21–4.10 (m, 4 H), 2.92 (s, 3 H), 1.51 (s, 3 H); mass spectrum, exact mass calcd for $C_{14}H_{16}O_3$ m/e 232.1099, obsd 232.1120.

28. Chromatography (2.5 cm × 25 cm column, 6% Et_2O/PE as eluant) gave **29** as a clear colorless oil: IR (neat) 2940 (s), 2840 (m), 1450 (s), 1400 (s), 1080 (s), 755 (s); ^1H NMR δ 5.90 (s, 4 H), 3.81 (s, 2 H), 3.12 (s, 3 H), 1.38 (s, 6 H), 1.31 (s, 3 H); mass spectrum, exact mass calcd for $C_{12}H_{18}O_3$ m/e 210.1256, obsd 210.1271.

Hydrolysis of *p*-Quinol Ether Ketals to *p*-Quinol Ethers. The hydrolysis procedure given for **5c** is representative of the method used for the hydrolysis of the remaining compounds, for which only the hydrolysis conditions, purification procedure, and spectroscopic data are given.

5c. The ketal **5c** (3.0 g, 0.011 mol) was dissolved in an acetone/water (2:1) solution (60 mL) and cooled to 0 °C. To this solution was added concentrated HCl (three drops), and the reaction mixture was stirred at 0 °C for 0.75 h. After 0.75 h, the dienone that had precipitated from the reaction solution was isolated by suction filtration and dried at 0.3 Torr for 6.0 h to afford **6c** (2.1 g, 83%) as a white crystalline solid: mp 112–114 °C; IR (KBr) 1670 (s), 1625 (m), 1610 (m), 1509 (s), 1255 (s), 1185 (sh), 1175 (m), 1075 (s), 1058 (s), 1026 (m), 851 (m), 831 (s); ^1H NMR δ 7.10 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 40 Hz, 4 H), 6.56 (AB q, J_{AB} = 9 Hz, $\Delta\nu$ = 35 Hz, 4 H), 3.77 (s, 3 H), 3.39 (s, 3 H); mass spectrum, exact mass calcd for $C_{14}H_{14}O_3$ m/e 230.0941, obsd 230.0932.

5a: acetone/10% HCl (3:2) at 0 °C for 0.5 h. Recrystallization from CH_2Cl_2/PE afforded **6a** as white crystals: mp 85–87 °C; IR (KBr) 2990 (m), 2939 (s), 2900 (m), 2805 (s), 1690 (sh), 1670 (s), 1635 (m), 1490 (m), 1460 (m), 1450 (s), 1401 (m), 1390 (m), 1210 (m), 1200 (m), 1178 (s), 1105 (s), 1090 (sh), 1070 (s), 1038 (s), 955 (s), 950 (s), 852 (m), 750 (s), 695 (s); ^1H NMR δ 7.50–7.24 (m, 4 H), 6.58 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 33 Hz, 4 H), 3.14 (s, 3 H); mass spectrum, exact mass calcd for $C_{13}H_{12}O_2$ m/e 200.0837, obsd 200.0834.

5b: acetone/10% HCl (3:1) at 0 °C for 1.5 h. Flash column chromatography on silica gel (1:1 C_6H_6/PE as eluant) gave **6b** as a light yellow solid; recrystallization from Et_2O gave **6b** as white needles: mp 87–88 °C; IR (KBr) 2990 (m), 2938 (m), 2830 (m), 1683 (s), 1660 (s), 1620 (s), 1601 (s), 1480 (s), 1460 (m), 1445 (m), 1390 (s), 1280 (m), 1168 (m), 1065 (s), 1059 (s), 940 (s), 916 (m), 860 (s), 759 (s), 721 (s), 710 (s), 455 (m), 430 (m), 345 (m); ^1H NMR δ 7.73–7.51 (m, 1 H), 7.24–7.15 (m, 3 H), 6.62 (AB q, J_{AB} = 11 Hz, $\Delta\nu$ = 20 Hz, 4 H), 3.33 (s, 3 H), 2.38 (s, 3 H); mass spectrum, exact mass calcd for $C_{14}H_{14}O_2$ m/e 214.0994, obsd 214.0984.

13a → 6a: acetone/10% HCl (1:1) at −5 °C for 10.0 h. Recrystallization from CH_2Cl_2/PE gave **6a** as white needles, mp 85–87 °C.

13b → 6b: acetone/10% HCl (1:1) at −5 °C for 10.0 h. Recrystallization from Et_2O gave **6b** as white needles, mp 87–88 °C.

13c → 6c: acetone/10% HCl (1:1) at −5 °C for 10.0 h. Recrystallization from Et_2O/PE gave **6c** as white needles, mp 112–114 °C.

18a → 19a: acetone/10% HCl (1:1) at 6 °C for 12.0 h. Chromatography on silica gel (30.0 g, 1.8 cm × 20 cm, 12% Et_2O/PE as eluant) gave **19a** as a crystalline solid, mp 60–62 °C (lit.[4a] mp 62–63 °C).

18b → 19b: acetone/10% HCl (1:1) at 6 °C for 12.0 h. Chromatography on silica gel (25.0 g, 1.8 cm × 20 cm, 10% Et_2O/PE as eluant) gave **19b** as a clear colorless oil, which crystallized at low temperature: mp 32–34 °C; IR (neat) 2987 (m), 2940 (s), 1685 (s), 1671 (s), 1638 (s), 1460 (m), 1395 (m), 1381 (m), 1270 (m), 1258 (m), 1085 (s, br), 911 (m), 858 (s), 701 (m); ^1H NMR δ 6.42 (AB q, J_{AB} = 11 Hz, $\Delta\nu$ = 29 Hz, 4 H), 3.11 (s, 3 H), 1.65 (q, J = 7 Hz, 2 H), 0.72 (t, J = 7 Hz, 3 H); mass spectrum, exact mass calcd for $C_9H_{12}O_2$ m/e 152.0838, obsd 152.0807.

18c → 19c: acetone/10% HCl (1:1) at 6 °C for 10.0 h. Chromatography on silica gel (25.0 g, 1.8 cm × 25 cm, 15% Et_2O/C_6H_6 as eluant) gave **19c** as a clear colorless oil, which crystallized at low temperature: mp 41–43 °C; IR (neat) 2975 (s), 2940 (m), 2830 (s), 1675 (s, br), 1640 (s), 1508 (s), 1469 (s), 1389 (s), 1310 (m), 1272 (s), 1230 (s), 1210 (s), 1168 (s), 1080 (s, br), 911 (s), 880 (s), 851 (s), 702 (s); ^1H NMR δ 6.47 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 28 Hz, 4 H), 3.10 (s, 3 H), 1.96 (septet, J = 9 Hz, 1 H), 0.83 (d, J = 7 Hz, 8 H); mass spectrum, exact mass calcd for $C_{10}H_{14}O_2$ m/e 166.0994, obsd 166.0991.

18d → 2-(4-methoxyphenoxy)ethanol: acetone/5% HCl (5:3) at 6 °C for 2.5 h. Recrystallization from hot PE gave the product as white needles, mp 62–64 °C (lit.[11] mp 63–65 °C).

18e → 19e: acetone/10% HCl (2:1) at 6 °C for 4.5 h. Chromatography on silica gel (20 g, 1.8 cm × 15 cm, 15% Et_2O/PE as eluant) gave **19e** as a clear colorless oil: IR (neat) 2939 (m), 2820 (m), 1675 (s), 1640 (s), 1612 (m), 1441 (m), 1390 (m), 1375 (m), 1299 (s), 1228 (m), 1211 (m), 1115 (s), 1070 (s, br), 1020 (m), 1003 (m), 975 (s), 884 (m); ^1H NMR δ 6.42 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 29 Hz, the higher field component meta-coupled, J = 2 Hz) and 6.07 (m, 3 H), 3.21 (s, 3 H), 1.87 (d, J = 1.5 Hz, 3 H), 1.42 (s, 3 H); mass spectrum, exact mass calcd for $C_9H_{12}O_2$ m/e 152.5437, obsd 152.5434.

21 → 22: acetone/10% HCl (2.4:2) at 6 °C for 4.5 h. Chromatography on silica gel (20.0 g, 1.8 cm × 20 cm, 18% Et_2O/PE) gave **22** as a clear, almost colorless oil, which crystallized at low temperature: mp 52–53 °C; IR (neat) 2935 (s), 1675 (s), 1605 (m), 1455 (s), 1380 (s), 1300 (s), 1240 (m), 1095 (s, br), 950 (m), 750 (s, br); ^1H NMR δ 8.16–8.06 (m, 1 H), 7.63–7.30 (m, 3 H), 6.7 (AB q, J_{AB} = 10 Hz, $\Delta\nu$ = 35 Hz, 2 H), 2.99 (s, 3 H), 1.57 (s, 3 H); mass spectrum, exact mass calcd for $C_{12}H_{12}O_2$ m/e 188.0837, obsd 188.0857.

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Registry No. **1** (R = H), 935-50-2; **1** (R = OCH_3), 64701-03-7; **2a**, 42860-77-5; **2b**, 110391-79-2; **2c**, 110391-80-5; **2e**, 110391-81-6; **2f**, 110391-82-7; **3a**, 92-69-3; **3b**, 38262-85-0; **3c**, 16881-71-3; **3d**, 17190-05-5; **3e**, 29886-65-5; **3f**, 37055-79-1; **4a**, 613-37-6; **4b**, 92495-54-0; **4c**, 2132-80-1; **4g**, 103594-11-2; **4h**, 103594-12-3; **4i**,

18110-71-9; **5a**, 103594-13-4; **5b**, 103594-14-5; **5c**, 103624-16-4; **5g**, 110391-83-8; **5h**, 103594-16-7; **6a**, 28093-86-9; **6b**, 103594-24-7; **6c**, 103594-23-6; **7**, 103594-26-9; **8**, 103594-27-0; **9**, 110392-00-2; **10**, 110392-03-5; **11**, 103594-17-8; **12a**, 19070-95-2; **12b**, 110391-84-9; **12c**, 103594-19-0; **12d**, 110391-85-0; **12e**, 103594-18-9; **12f**, 110391-86-1; **13a**, 103594-20-3; **13b**, 110391-87-2; **13c**, 103594-22-5; **13e**, 103594-21-4; **14**, 110391-88-3; **15b**, 14202-49-4; **16b**, 110391-99-6; **17a**, 15149-10-7; **17b**, 54411-10-8; **17c**, 54576-35-1; **17d**, 713-46-2; **17e**, 34221-43-7; **17f**, 85983-26-2; **18a**, 110391-89-4; **18b**, 110391-90-7; **18c**, 110391-91-8; **18d**, 110391-92-9; **18e**, 110391-93-0; **19a**, 23438-17-7; **19b**, 110391-94-1; **19c**, 110391-95-2; **19d**, 5394-57-0; **19e**, 55153-55-4; **20**, 110392-01-3; **21**, 110392-02-4; **22**, 72054-91-2; **28**, 110391-96-3; **29**, 110391-97-4; 2-$H_3CC_6H_4Li$, 6699-93-0; 4-$H_3COC_6H_4Li$, 14774-77-7; 3,4-$(H_3CO)_2C_6H_3Li$, 80245-51-8; 2-$BrC_6H_4CH_3$, 95-46-5; 4-$BrC_6H_4OCH_3$, 104-92-7; 3,4-$(CH_3O)_2C_6H_3I$, 5460-32-2; HO-*p*-$C_6H_4C_6H_4$-*o*-CH_3, 38262-85-0; H_3CO-*p*-$C_6H_4C_6H_4$-*o*-CO_2H, 18110-71-9; H_3CO-*p*-$C_6H_4C_6H_4$-*o*-CH_2OH, 110391-98-5; H_3CO-*p*-$C_6H_4C_6H_4$-*o*-CHO, 16064-04-3; 4-$H_3CC_6H_4OH$, 106-44-5; 4-EtC_6H_4OH, 123-07-9; 4-*i*-PrC_6H_4OH, 99-89-8; 4-*t*-BuC_6H_4OH, 98-54-4; 4-$PhCH_2C_6H_4OH$, 101-53-1; 4-$H_3CC_6H_4OCH_2CO_2H$, 940-64-7; 4-$H_3CC_6H_4OCH_2CO_2CH_3$, 38768-63-7; CD_3I, 865-50-9; 3,4-$(CH_3)2C_6H_4OH$, 95-65-8; 2-lithiothiophene, 2786-07-4; 4-methylnaphthol, 10240-08-1; ethylene carbonate, 96-49-1.

Supplementary Material Available: Experimental details for preparation of starting materials, ^1H NMR decoupling experiments and ^1H NMR spectra for **8** and **11**, and COSY 45 ^1H NMR spectrum for **11** (14 pages). Ordering information is given on any current masthead page.

An ab Initio Theoretical Study of the Base-Induced Ring Opening of Ethene Episulfoxide

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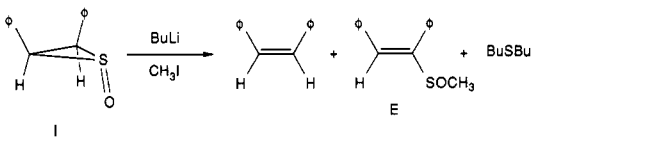
The ring opening of the syn and anti carbanions of ethene episulfoxide has been studied at the Hartree–Fock level with complete geometry optimization by using a minimal STO-3G* basis and a 3-21G basis augmented by diffuse sp functions on all heavy atoms plus d orbitals on sulfur. Relative energies were calculated with second order Møller–Plesset perturbations theory with the larger basis set. The two carbanions have about the same stability, but ring opening is much easier from the syn form. The inversion barrier for the anti–syn interconversion is slightly lower than the barrier for the ring opening of the anti carbanion and significantly higher than the barrier for the ring opening of the syn carbanion. The low barrier for ring opening of the syn carbanion is consistent with the higher yield and retention of stereochemistry observed in the organolithium mediated ring opening of cis-substituted episulfoxides. Inversion competing with ring opening accounts for the partial loss of stereospecificity observed in the trans-substituted episulfoxides.

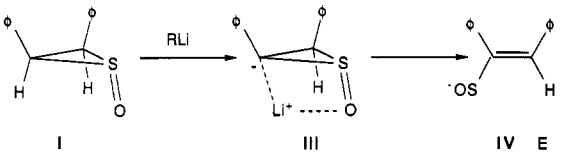
Organolithium derivatives can react with episulfoxides to give products due to attack both on sulfur and on hydrogen.[2,3] *cis*- (I) and *trans*- (II) stilbene episulfoxides, treated with butyllithium in ether at temperatures ranging from 0 to −78 °C, result in desulfurization and ring opening (Scheme I). Desulfurization proceeds via alkyl attack on the sulfur to form an oxysulfurane, which decomposes stereospecifically to the olefin.[2,3] Ring opening occurs by deprotonation to form a carbanion. In the case of *cis*- (I) and *trans*- (II) stilbene episulfoxides, the yields of ring-opening products were 31% and 1.5%, respectively. The *cis*-stilbene episulfoxide (I) ring opening is stereospecific, but the *trans*-stilbene episulfoxide (II) shows a partial loss of stereospecificity (formation of the *E* isomer).

In the ring opening, the base must attack one of the hydrogens. For *cis*-stilbene episulfoxide (I), hydrogen abstraction can produce only the syn carbanion III (Scheme II). This carbanion, possibly stabilized by chelation of Li^+, opens to give the ethenesulfenate anion IV, which is then alkylated by methyl halide. On the other hand, *trans*-stilbene episulfoxide (II), which has more hindered hydrogens and gives a poorer yield from ring opening, has two possible sites for deprotonation (Scheme III). Abstraction of the hydrogen syn to the oxygen leads to the syn carbanion V, which opens stereospecifically to the *Z* isomer VII. Abstraction of the other hydrogen produces a carbanion anti to the oxygen (VI), which can also open stereospecifically to the *Z* isomer VII. Differences in the kinetic acidity of the two hydrogens will determine the ratio of the syn and anti carbanions. However, the presence of the *E* isomer cannot be explained by dif-

Scheme I



Scheme II



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