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Intramolecular Anodic Carbon−Carbon Bond Formation from Oxidized Phenol Intermediates. Effect of Oxygenated Substituents on the Yields of Spiro Dienones in Electrochemical and Iodobenzene Diacetate Oxidations

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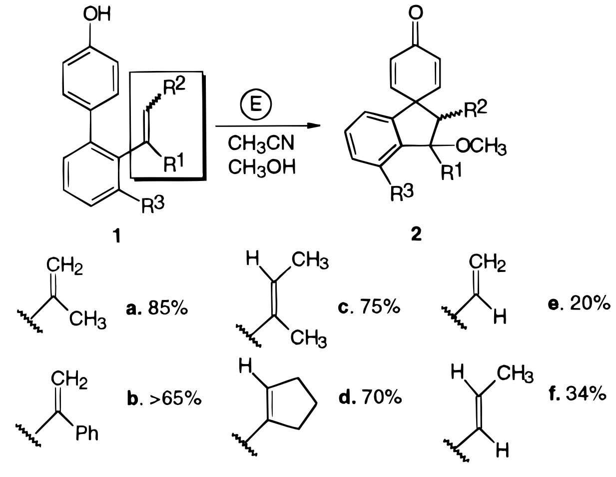
The single-cell, constant-current anodic oxidation of a series of 4-(2-alkenylaryl)phenols was studied in which the aryl substituents were 2-vinyl-4,5-dimethoxy, **6a**; 2-propenyl-4,5-dimethoxy, **9a**; 2-vinyl-4,5-methylenedioxy, **6b**; 2-propenyl-4,5-methylenedioxy, **9b**; 2-vinyl-4-methoxy, **6c**; 2-propenyl-4-methoxy, **9c**; 2-vinyl-5-methoxy, **6d**; and 2-propenyl-5-methoxy, **9d**. Two compounds having methoxyl groups on the phenolic ring were also studied: 4-(2′-propenylphenyl)-2-methoxyphenol, **9e**, and 4-(2′-propenylphenyl)-3-methoxyphenol, **9f**. A novel synthetic route to the methoxy compounds **6c**, **9c**, **6d**, and **9d** was developed. This involved as a key step the MAD, bis(2,6-di-*tert*-butyl-4-methylphenoxide)methylaluminum, mediated addition of organolithium and Grignard reagents to functionalize quinol ether derivatives. Anodic oxidation of compounds **6a**, **9a**, **9b**, **6c**, **9c**, and **9d** gave good yields of spiro dienones arising from trapping of the phenoxonium ion by the alkenyl side chain followed by reaction of the resulting cation with methanol. The products from the electrochemical oxidation of these 4-(2′-alkenylaryl)phenols were compared with those obtained from the iodobenzene diacetate oxidations. In general, the compounds that gave good yields of spiro dienones from electrochemical oxidation gave good yields from iodobenzene diacetate oxidations. However, there were two cases in which the results of the two oxidations did not parallel each other. Whereas anodic oxidation of **9f** gave a low yield of spiro dienone, the iodobenzene diacetate route gave a 74% yield of this product. In the case of **9d**, the opposite effect was noted: the electrochemical route gave a higher yield than did the iodobenzene diacetate oxidation.

Mild methods for the formation of carbon−carbon bonds are central to the synthesis of compounds having sensitive functional groups. Electrochemistry offers such a method, and we have been investigating the anodic carbon−carbon bond-forming reactions arising from phenoxonium ion intermediates.[1−3] The oxidative conversion of 4-(2′-alkenylphenyl)phenols to spiro dienones, **1** → **2**, was initially chosen for study because this system would allow a systematic study of the influence of electronic and steric factors on the yield of the carbon−carbon bond-forming process.[1] Previously, we reported that olefinic substituents can markedly alter the yield of the cyclization reaction.[1c] A particularly striking effect resulted from the replacement of an alkyl group with hydrogen at the α-position of the alkenyl side chain: compare the yields of **2** from **1a**−**d** versus **1e,f**. The nature of this substituent effect is unknown. However, **1g** ($R_1 = R_2 =$ H, $R_3 = CH_3$) does furnish the cyclization product **2h** in good yield (70% compared to 20% yield for **1e**), establishing that a buttressing effect can enhance the yield on the spiro dienone product.[1d]



R^3 = H for **1a-f**; R^3 = CH_3 for **1g**

We report in this paper synthetic routes to methoxyl-substituted 4-(2′-alkenylphenyl)phenols and a study of their oxidative cyclization chemistry. The substitution of methoxyl for hydrogen on the aromatic rings can markedly influence the yield of the spiro dienone formed in the oxidative cyclization.

Preparation of 4-(2′-Alkenylaryl)phenols. A most direct route to these compounds involves organolithium addition to a quinone dimethyl ketal followed by ketal hydrolysis and reduction. Although the bromostyrene derivative **4** was easily prepared in good yield via the Peterson reaction on the bromo aldehyde **3**, **4** was quite unstable to storage and appeared to easily polymerize under the metalation conditions. Reaction of the lithium compound derived from **4** with the dimethyl ketal of

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[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1996.

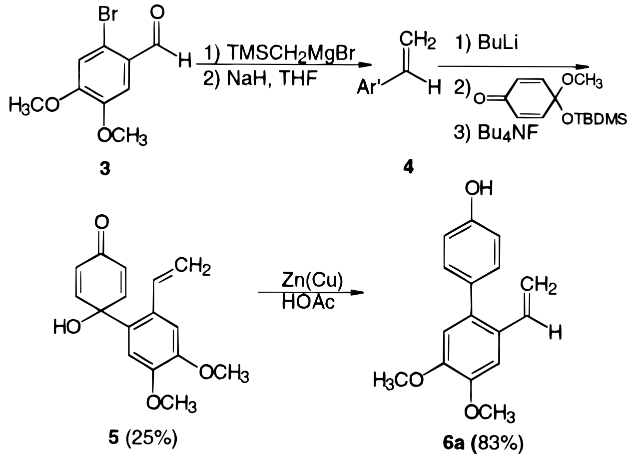
(1) (a) Morrow, G. W.; Swenton, J. S. *Tetrahedron Lett.* **1987**, *28*, 5445. (b) Callinan, A.; Chen, Y.; Morrow, G. W.; Swenton, J. S. *Ibid.* **1990**, *31*, 4551. (c) Morrow, G. W.; Chen, Y.; Swenton, J. S. *Tetrahedron* **1991**, *47*, 655. (d) Swenton, J. S.; Carpenter, K.; Chen, Y.; Kerns, M. L.; Morrow, G. W. *J. Org. Chem.* **1993**, *58*, 3308.

(2) For general references concerning the oxidation chemistry of phenols, see the literature cited in ref 1.

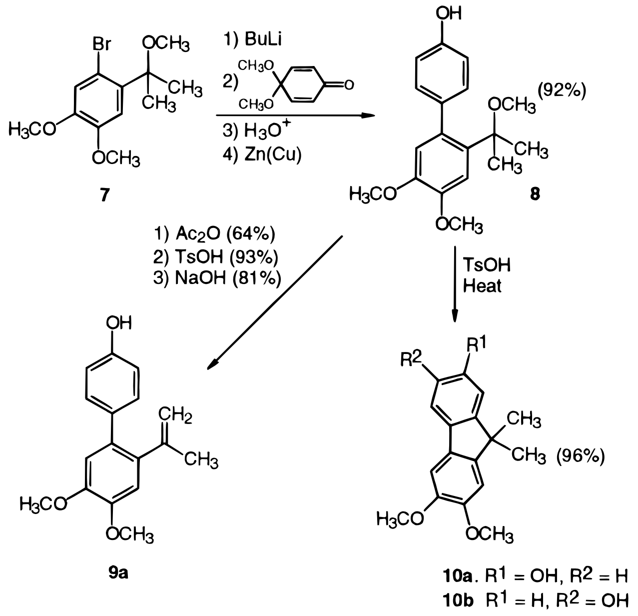
(3) For recent examples of and leading references to anodic carbon−carbon bond-coupling reactions, see: (a) Maki, S.; Asaba, N.; Kosemuar, S.; Yamamura, S. *Tetrahedron Lett.* **1992**, *33*, 4169. (b) Yamamura, S.; Shizuri, Y.; Shigemori, H.; Yoshishige, O.; Mitsuru, O. *Tetrahedron* **1991**, *47*, 635. (c) Moeller, K. D.; Tinao, L. V. *J. Am. Chem. Soc.* **1992**, *114*, 1033.

0022-3263/96/1961-1267$12.00/0

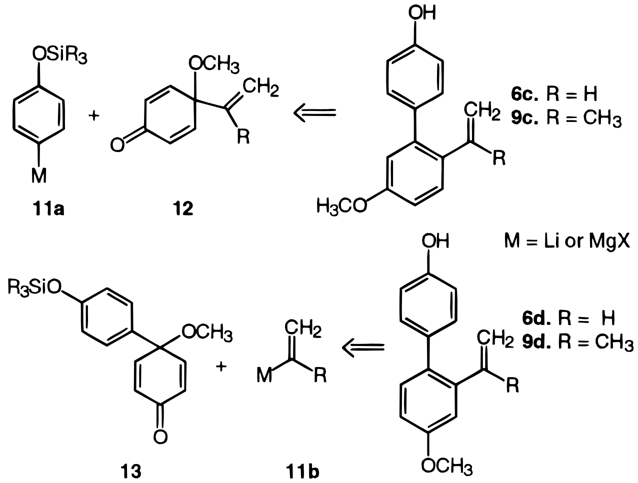
benzoquinone followed by hydrolysis of the dimethyl ketal and reduction did not lead to **5**.[4] However, by using the *tert*-butyldimethylsilyl methyl ketal, **5**[5] was prepared and then reduced to the desired 4-(2′-alkenylaryl)phenol **6a**. The low yield for the **4** → **5** conversion is probably related to the ease of polymerization of the starting bromostyrene derivative **4**.



The stability problems associated with the bromostyrene **4** prompted using a lithiated aromatic derivative having the olefin in latent form. Thus, for the preparation of **9a**, the carbon–carbon bond-forming step was reaction of the lithium reagent derived from **7** with the dimethyl ketal of quinone followed by hydrolysis and reduction to form **8**. Attempted elimination of methanol from **8** gave a fluorene derivative (96%) which undoubtedly arose from trapping of the benzylic carbonium ion to yield a dienone followed by dienone–phenol rearrangement. An NOE experiment allowed a clear distinction between structures **10a** and **10b** for this rearrangement product. The ^{1}H NMR (500 MHz) spectrum showed the following: δ 7.46 (d, $J = 10$ Hz, 1 H), 7.15 (s, 1 H), 6.92 (s, 1 H), 6.88 (d, $J = 2$ Hz, 1 H), 6.78 (dd, $J = 10$, 2 Hz, 1H), 3.94 (s, 3 H), 3.92 (s, 3 H), 1.41 (s, 6 H). When the singlet at δ 1.4 was irradiated, only the singlet at δ 6.92 and the doublet at δ 6.88 showed enhancement. The *meta*-coupled doublet at δ 6.88 must be the proton adjacent to both the phenolic hydroxyl and the ring carbon. This proton would show an NOE enhancement only in **10a**, where it is close to the *gem*-dimethyl group. The rearrangement problem could be avoided if the phenol were first converted to its acetate and then the methanol eliminated from the tertiary methyl ether by TsOH, followed by basic hydrolysis of the acetate, **8** → **9a**. The four-step sequence **7** → **8** proceeded in excellent yield. A similar series of reactions was used to prepare the methylenedioxy derivatives, **6b** and **9b**, using piperonal as starting material (see supporting information for details).



Scheme 1. Strategy to Methoxyl-Substituted 4-(2-Alkenylphenyl)phenols



The route **7** → **8** → **9** was especially convenient since the 2-bromobenzaldehyde derivatives required for the synthesis were available from bromination of 3,4-dimethoxybenzaldehyde and piperonal. This basic synthetic approach was also employed for the preparation of **9g,h** (*vide infra* and supporting information). However, for the remaining compounds, **6c,d** and **9c,d**, desired for study, the required bromo aldehyde derivatives were not easily available. These compounds required a different synthetic approach.

A general route to the required 4-arylphenol derivatives is outlined in Scheme 1. The quinol derivatives **12** and **13** would be prepared via organometallic addition to a quinone ketal, followed by methylation and ketal hydrolysis. The critical feature in implementing this synthetic strategy was a high-yield procedure for effecting conjugate addition of organometallic reagents to quinone and quinol ketal derivatives. Until our application[6,7] of the bis(2,6-di-*tert*-butyl-4-methylphenoxide)methylaluminum (MAD) mediated addition of organolithium and Grignard reagents to functionalization of quinone and

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[4] (a) The acid-catalyzed reaction of the quinol derivative affords a phenanthrene: Stern, A. J.; Swenton, J. S. *J. Org. Chem.* **1988**, *53*, 2465. (b) This chemistry has been optimized to a useful synthesis of phenanthrenes: Marks, T. M.; Morrow, G. W. *Tetrahedron Lett.* **1992**, *33*, 2269.

[5] Stern, A. J.; Swenton, J. S. *J. Org. Chem.* **1987**, *52*, 2763.

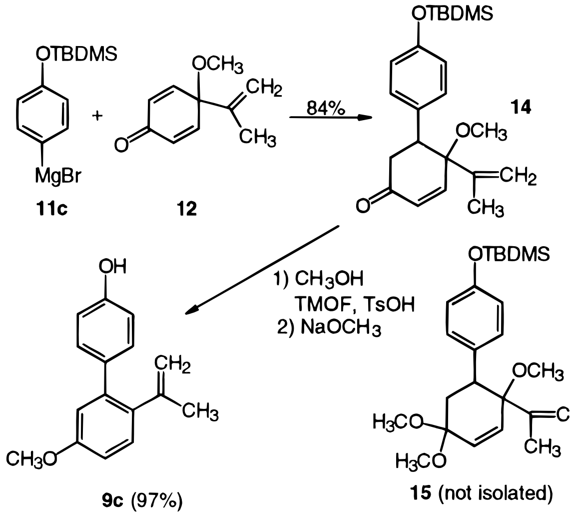
[6] (a) Stern, A. J.; Swenton, J. S. *J. Chem. Soc., Chem. Commun.* **1988**, 1255. (b) Stern, A. J.; Rohde, J. J.; Swenton, J. S. *J. Org. Chem.* **1989**, *54*, 6156.

[7] When this method was applied to conjugate additions of alkyllithium reagents to enones,[8] poor yields were obtained. The difference between additions to enones and the work herein is undoubtedly the directive effect of the ether linkages at the 4-position of these quinol ether derivatives.

[8] Maruoka, K.; Nonoshita, K.; Yamamoto, H. *Tetrahedron Lett.* **1987**, *28*, 5723.

quinol derivatives, effecting this conversion was problematical.[9] However, employing this conjugate addition reaction as the key step resulted in the synthesis **6c,d** and **9c,d**. This chemistry comprises a unique approach to 4-(2-alkenylaryl)phenols. An especially convenient feature of this strategy is the use of the same organometallic reagents in the synthesis of the pairs **6c,d** and **9c,d**, the only difference being the order of introduction of the organometallic carbon segment.

The successful route employing the strategy outlined in Scheme 1 is given below for the preparation of **9c**. Compounds **6c,d**, and **9d** were prepared with a similar series of reactions, and the details are given in the supporting information. Several comments are in order. First, the MAD was prepared by slow addition of trimethylaluminum to a solution of 2,6-di-*tert*-butyl-4-methylphenol in toluene or methylene chloride. It was discovered after the majority of this work had been done that improved yield of the conjugate addition resulted if the MAD solution was kept at −78 °C until the solution turned a milky yellow. Then, the quinol ether derivative was added to form the complex followed by addition of the organometallic reagent. The conversion **14** → **9c** was performed by first heating with trimethyl orthoformate, which presumably forms the ketal **15**, followed by thermal elimination of methanol and finally desilylation of the silyl ether to give **9c**.

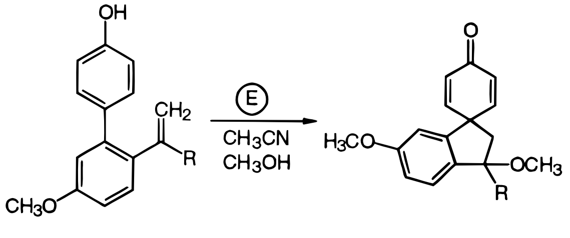


11c **12** **14**

9c (97%) **15** (not isolated)

Anodic Oxidation Studies. Except where noted, all electrochemical oxidations were conducted in 4:1 CH_3CN/CH_3OH in a single-celled apparatus using a platinum gauze anode and a platinum sheet or wire cathode. The reactions were followed by either TLC or reverse-phase HPLC and terminated when all starting phenol had reacted. Products were isolated by conventional chromatography. The oxidative cyclization chemistry of the dioxygenated derivatives **6a,b** and **9a,b** was of special concern since this oxygen substitution pattern occurs in spirocyclic natural products such as cannabispiradienone,[10a] oxocrinine,[10b] orientalinone,[10c] and pretazzetine.[10d] These oxidative cyclizations might be useful as key carbon−carbon bond-forming steps in the syntheses of these compounds. However, it is instructional to first discuss the oxidative chemistry of the monooxygenated derivatives **6c,d** and **9c,d**.

Previously, we showed that the yield of cyclization product improved with alkyl substitution on the styrene-like double bond. Thus, if the nucleophilicity of the double bond played an important role in determining the yield of the cyclization, substituents on the aromatic ring which increased the nucleophilicity of the double bond would increase rate of the cyclization reaction and thus raise the yield of the spiro dienone. By this reasoning, the methoxy derivatives **6c** and **9c** should increase the yields of the cyclization product. Indeed, anodic oxidation of **6c** and **9c** furnished spiro dienones **16c** and **17c** in yields of 47% and 84%, respectively. The yield for the **6c** → **16c** reaction, even when uncorrected for recovered starting material, is over twice that for the parent system, **1e** → **2e**. When the **6c** → **16c** reaction was conducted to complete conversion of **6c**, **16c** was partly converted to another product;[11] thus, this limits the preparative aspect of the reaction. However, the methoxy group in this system must be increasing the rate of the cyclization reaction relative to other competing reactions.



6c (R = H)
9c (R = CH_3)

16c (R = H, 47%)
17c (R = CH_3, 84%)

Simple considerations do not allow a clear rationale as to how the methoxy group in **6d** and **9d** will affect the yield of the oxidative cyclization product. From an inductive standpoint, the methoxy group *meta* to the alkenyl side chain would make the double bond less nucleophilic. However, the methoxy group could stabilize the phenoxonium ion intermediate, increasing its lifetime, thus increasing the rate for reaction with the alkenyl side chain. Anodic oxidation of **6d** gave the quinol ether **18d** (70%); no spiro dienone product akin to **16d** could be detected. The anodic oxidation of **9d** again showed the dramatic effect of the methyl substituent on the course of the oxidative cyclization as **17d** was formed in 80% yield.

In the 4,5-dimethoxy and 4,5-methylenedioxy derivatives **6a,b** and **9a,b**, the substituents exert opposing effects. The oxygen group *para* to the styrene-like double bond would increase the electron density at the olefinic linkage. However, the oxygen substituent *para* to the aryl ring would be slightly deactivating relative to the styrene double bond. Although anodic oxidation of both **9a,b** gave the expected spiro dienones **17a** (92%) and **17b** (70%), the results for the analogues **6a,b** differed. For **6a**, the spiro dienone **16a** was formed in 70% yield, whereas for **6b**, the spiro dienone **16b** was isolated in

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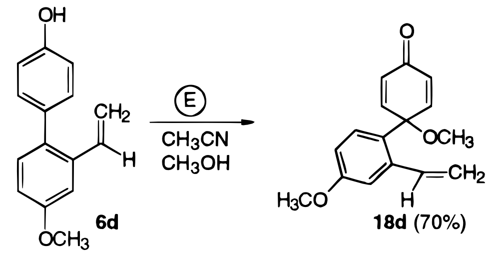
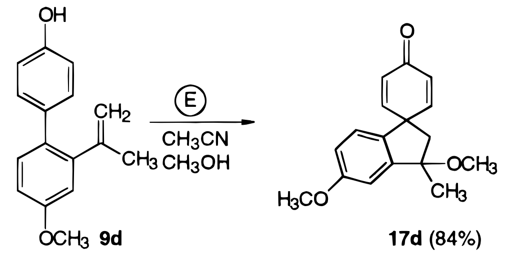
[9] (a) Nilsson, A.; Ronlan, A. *Tetrahedron Lett.* **1975**, 1107. (b) Henton, D. R.; Anderson, K.; Manning, M. J.; Swenton, J. S. *J. Org. Chem.* **1980**, *45*, 3422. (c) Semmelhack, M. F.; Keller, L.; Sato, T.; Speiss, E. *Ibid.* **1982**, *47*, 4382. (d) Semmelhack, M. F.; Keller, L.; Sato, T.; Speiss, E.; Wulff, W. *Ibid.* **1985**, *50*, 5566.

[10] (a) Crombie, L.; Crombie, W. M. L.; Jamieson, S. V. *Tetrahedron Lett.* **1979**, 661. (b) Kotani, E.; Kitizawa, M.; Tobinanga, S. *Tetrahedron* **1972**, *30*, 3027. (c) Battersby, A. R.; Brockson, T. J.; Ramage, R. *J. Chem. Soc., Chem. Commun.* **1969**, 464. (d) Tsuda, Y.; Ukai, A.; Isobe, K. *Tetrahedron Lett.* **1972**, 3153.

[11] The product formed in this reaction had spectroscopic properties in agreement with those of **16c** (R = OCH_3) which would arise from benzylic oxidation of **16c** (R = H). However, the compound was not rigorously characterized.

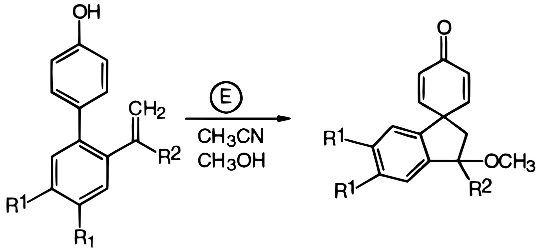


6d → **18d** (70%)



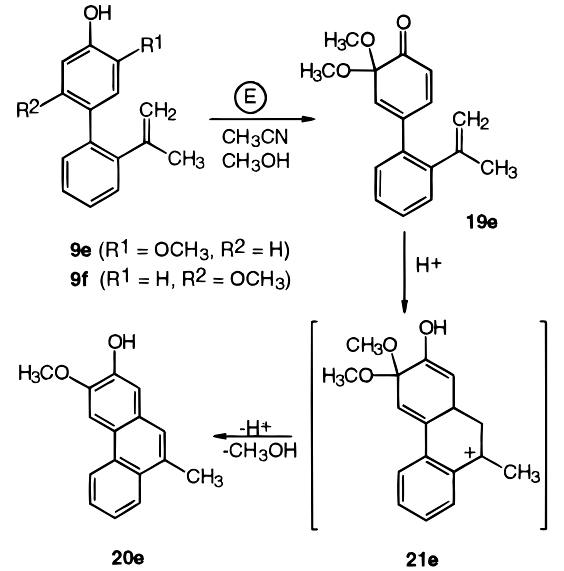
9d → **17d** (84%)

only 12% yield. Again, the effect of methyl substitution on the double bond in **9a,b** results in a good yield of the spiro dienones; however, without the methyl group the result is less predictable. Unfortunately, there is no information on the competing reactions for the **6b** reaction since no other products could be characterized; only noncharacterized highly polar material was isolated by chromatography. The obvious difference between the 4,5-dimethoxy substituent and the 4,5-methylenedioxy group in **6a,b** is the stereoelectronic relationship between the electron pairs on the oxygen and the *p*-orbitals of the benzene ring. The five-membered methylenedioxy group does not have the flexibility to optimize the overlap of the oxygen lone pairs with the π-system. This means that the methylenedioxy group would not be so effective at enhancing the electron density on the styrene double bond as a 4,5-dimethoxy group.



6a ($R^1 = OCH_3$, $R^2 = H$)	**16a** ($R^1 = OCH_3$, $R^2 = H$) 70%
6b ($R^1 = OCH_2O$, $R^2 = H$)	**16b** ($R^1 = OCH_2O$, $R^2 = H$) 12%
9a ($R^1 = OCH_3$, $R^2 = CH_3$)	**17a** ($R^1 = OCH_3$, $R^2 = CH_3$) 92%
9b ($R^1 = OCH_2O$, $R^2 = CH_3$)	**17b** ($R^1 = OCH_2O$, $R^2 = CH_3$) 70%

The remaining two compounds studied were substituted with methoxy groups at the 2- and 3-positions of the phenolic ring. Anodic oxidation of **9e** followed by silica gel chromatography gave **19e** (26%)[12] and **20e** (39%). The phenanthrene **20e** is formed from rearrangement of **19e** on silica gel, probably via the carbonium ion **21e**. So **20e** is probably not a product from the electrochemically produced phenoxonium ion. Disappointingly, anodic oxidation of **9f** gave a complex product mixture from which no pure products could be obtained. Thus, the electrochemical oxidation of **9e,f** affords no spiro dienone product; however, see the discussion of iodobenzene diacetate oxidation of **9f** below.

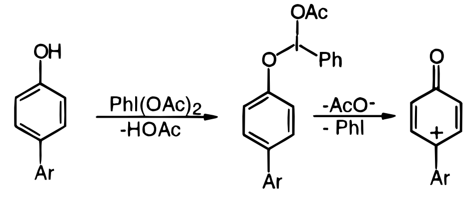


9e ($R^1 = OCH_3$, $R^2 = H$)
9f ($R^1 = H$, $R^2 = OCH_3$)

19e

20e **21e**

Iodobenzene Diacetate Oxidation of Phenols. For most electrochemical reactions there are chemical oxidants which will effect the same conversion. The oxidation of phenols by iodobenzene diacetate to form various quinol and quinone derivatives has been reported previously.[1b,13−15] The initial step in the reaction is probably an exchange reaction between the phenol and iodobenzene diacetate to give an (aryloxy)iodonium acetate intermediate. Either **23** or the phenoxonium ion **24**, generated by loss of acetate and iodobenzene from **23** is the reactive intermediate in these oxidations. Table 1 compares the products and yields from electrochemical and iodobenzene diacetate oxidations of 4-(2-alkenylaryl)-phenols reported herein. In general, the phenols which gave high yields of spiro dienones in the electrochemical oxidation also gave good yields in the iodobenzene diacetate oxidations. There are two cases in which the yields from the electrochemical and chemical oxidations differ substantially. In the first case, the phenol **9d** gave the spiro dienone **17d** in 80% yield via electrochemical oxidation, but in only 24% yield by oxidation with iodobenzene diacetate. In the second case, the phenol



22 **23** **24**

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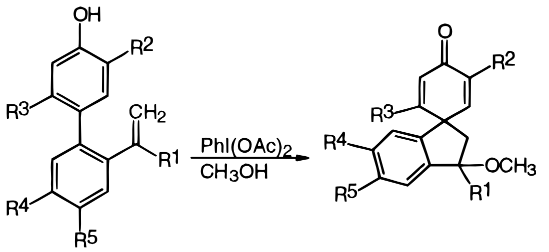
[12] The stability of **19e** with respect to dimerization is probably related to the steric effect of the 4-aryl substituent. For a discussion, see: Andersson, G.; Bertsson, *Acta Chem. Scand., Ser. B* **1975**, *29*, 948. Andersson, G. *Ibid.* **1976**, *30*, 64.

[13] For iodobenzene diacetate oxidation of phenols to quinone monoketals, see: (a) Peiter, A.; Elgendy, S. *Tetrahedron Lett.* **1988**, *29*, 677. (b) Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *J. Org. Chem.* **1987**, *52*, 3927. (c) Fleck, A. E.; Hobart, J. A.; Morrow, G. W. *Synth. Commun.* **1992**, *22*, 179.

[14] For phenolic coupling reactions with positive iodine reagents, see: Szantay, C.; Blasko, G.; Barczai-Beke, Pechy, P.; Dornyei, G. *Tetrahedron Lett.* **1980**, *21*, 3509. Rama Krishna, K. V.; Sujatha, K.; Kapil, R. S. *Ibid.* **1990**, *31*, 1351. Kita, Y.; Yakura, T.; Tohma, H.; Kikuchi, K. *Tetrahedron Lett.* **1989**, *30*, 1119.

[15] For nonoxidative methods for generating phenoxonium ions, see: Mortlock, S. V.; Seckington, J. K.; Thomas, E. J. *J. Chem. Soc., Perkin Trans.* **1988**, 2305. Abramovitch, R. A.; Alvernhe, G.; Bartnik, R.; Dassanayake, N. L.; Inbasekaran, M. N.; Kato, S. *J. Am. Chem. Soc.* **1981**, *103*, 4558. Shudo, K.; Orihara, Y.; Ohta, T.; Okamota, T. *J. Am. Chem. Soc.* **1981**, *103*, 943 and references cited therein.

Table 1. Comparison of Yields from $PhI(OAc)_2$ and Electrochemical Oxidation of Phenols

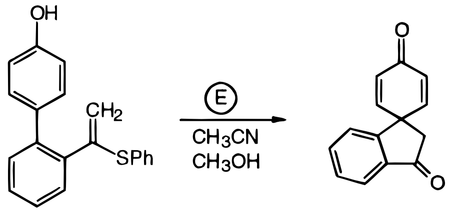


						yield, %	
phenol	R^1	R^2	R^3	R^4	R^5	Ⓔ	$PhI(OAc)_2$
1a	Me	H	H	H	H	67	85
1d	H	H	H	H	H	*a*	22
6a	H	H	H	OMe	OMe	50	70
9a	Me	H	H	OMe	OMe	76	92
6b	H	H	H	OCH_2O		23	12[b]
9b	Me	H	H	OCH_2O		79	70
6c	H	H	H	OMe	H	56	47[c]
6d	H	H	H	H	OMe	*a*	*a,d*
9d	Me	H	H	H	OMe	80	24
9e	Me	OMe	H	H	H	*a*	*a,d*
9f	Me	H	OMe	H	H	*a*	74

[a] The product was not detected. [b] The quinol ether **18b** (9%) was formed. [c] The quinol ether **18c** (34%) was formed. [d] The *o*-quinone monoketal **18e** (65%) was formed.

9f afforded the spiro dienone **17f** in 74% via reaction with iodobenzene diacetate, but this product was not detected in the electrochemical oxidation. We have no rationale for the differences in yields for the chemical versus electrochemical oxidations of these two compounds. However, it should be noted that the same intermediate is not necessarily formed in these two oxidations.

Anodic Cyclization of 4-[2-(1-(Phenylthio)vinyl)-phenyl]phenol (25). Except for **1h** and **6a**, the yield of the anodic cyclization products is much lower when the vinyl group is unsubstituted. This lower yield of the cyclization reaction for these compounds could be due to (1) a conformational effect wherein the olefinic group is less favorably disposed to cyclization with short-lived phenoxonium intermediate;[1d] (2) the absence of an electron-donating group on the olefinic group; or (3) a combination of (1) and (2). The low yields for oxidative cyclizations of compounds having unsubstituted side chains are a limitation of the potential synthetic use of the reaction. Recent research has shown the vinyl sulfide group to be a superb partner in bimolecular anodic carbon−carbon bond-forming reactions.[16c] The vinyl sulfide group in **25** would have a favorable conformational effect on the reaction but would also serve as an electron-donating group on the olefinic linkage. Thus, the vinyl sulfide **25** was prepared (79%) from the corresponding ketone, thiophenol, and titanium tetrachloride. Anodic oxidation of **25** in the usual way followed by silica gel chromatography gave the dione **26** (72%). Apparently, the mixed phenylthiomethyl ketal formed in the reaction undergoes hydrolysis under the workup/isolation conditions to afford the corresponding ketone. The use of the vinyl sulfide side chain allows preparation of a spiro dienone lacking an alkyl substituent in the five-membered ring. Although the two carbonyl groups in the product must be differentiated chemically to fully use the carbonyl group for further manipulation, the use of the vinyl sulfide group potentially markedly extends the scope of the chemistry.



25 **26** (72%)

Summary. This study has further defined the working hypothesis that the carbon−carbon bond-forming reactions involving intramolecular trapping of phenoxonium ions depends on the nucleophilic character of the double bond. Aromatic substituents which increase the nucleophilic character by resonance interaction increase the yield of spiro dienenone product. However, an alkyl group on the α-position of the 2-alkenyl substituent still has a dominating effect on the yield of the spiro dienone. Thus, 4-(2-alkenylaryl)phenols **6b** and **6d**, which have unsubstituted double bonds at the 2-position, give low or no yields of the spiro dienone product under oxidative conditions, whereas their analogues, **9b** and **9d**, having an α-methyl substitution on the olefinic side chain, gave excellent yields of the respective spiro dienones. As noted in the preceding section, a vinyl sulfide-substituted double bond (**25** → **26**) undergoes the anodic cyclization reaction in good yield, forming a product which does not have alkyl substitution in the five-membered ring. If this effect were general, the requirement of having an α-substituent on the double bond for a good yield of spiro dienone would be circumvented. With general routes to 4-(2-alkenylaryl)phenols now available, this chemistry complements photochemical[17a] and thermal routes[17b] to these spiro dieneone ring systems.

Unfortunately, we have been unable to establish all of the side reactions in the systems which do not give good yields of spiro dienones. Quinol ethers arising from addition of methanol to the oxidized phenol were characterized in some reactions; however, there was never a good accounting of material in these cases. Finally, the information obtained concerning structural features which promote the intramolecular carbon−carbon bond-forming reactions in 4-(2-alkenylaryl)phenols led to the design of high-yield bimolecular carbon−carbon bond-forming reactions of phenoxonium ions.[16] These results should serve as a useful guide in developing other carbon−carbon bond-forming reactions of phenoxonium and nitrenium ions.[18]

Experimental Section

General Procedures. Melting points were determined in capillaries and are uncorrected. Only strong absorptions are reported for IR spectra unless otherwise noted. ^1H NMR spectra were measured at the indicated frequency in $CDCl_3$ unless noted otherwise. All reagents or compounds not

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[16] For extensions of these model studies to bimolecular anodic carbon−carbon bond formation via phenol oxidations, see: (a) Wang, S.; Gates, B. D.; Swenton, J. S. *J. Org. Chem.* **1991**, *56*, 1979. (b) Gates, B. D.; Dalidowicz, P.; Tebben, A.; Wang, S.; Swenton, J. S. *Ibid.* **1992**, *57*, 1992. (c) Kerns, M. L.; Conroy, S. M.; Swenton, J. S. *Tetrahedron Lett.* **1994**, *35*, 7529.

[17] (a) Wang, S.; Morrow, G. W.; Swenton, J. S. *J. Org. Chem.* **1989**, *54*, 5364. See also ref 20. (b) Swenton, J. S.; Callinan, A.; Wang, S. *J. Org. Chem.* **1992**, *56*, 78.

[18] Dalidowicz, P.; Swenton, J. S. *J. Org. Chem.* **1993**, *58*, 4802.

[19] Kahovec, L.; Wanger, J. *Monatsch.* **1943**, *74*, 279.

explicitly referenced were obtained from commercial sources. Alumina and silica gel (Kiesel gel 60 230−400 mesh) were obtained from E. Merck Co. TLC was done using Merck silica gel 60 F_{254} precoated aluminum-backed plates, 0.2-mm thickness. All organometallic reactions were done under N_2 or Ar. Visualization was by UV or by spraying with 5% ethanolic phosphomolybdic acid and then heating. THF was purified by distillation from benzophenone ketyl. Throughout the Experimental Section, the following abbreviations are used: petroleum ether, bp 35−60 °C (PE), *p*-toluenesulfonic acid (*p*-TsOH). Extractive workup refers to extraction of the material into the indicated solvent, washing the organic layer with brine solution, drying over Drierite ($CaSO_4$), concentration in vacuo, and drying to constant weight under vacuum (1−2 Torr). The anodic oxidations employed a Kepco Model JQE 0-36V direct-current power supply. The anode was a cylindrical, perforated platinum sheet (4.8 cm × 2.5 cm diameter) with an estimated surface area of 60 cm^2. Using a current of 0.05 A corresponded to a current density of 0.84 mA/cm^2. The cathode was either a coil of copper wire (∼2.5 cm length) or a platinum wire (∼2 cm length) as specified. All anodic oxidations were performed at 0−10 °C. The current efficiencies are based on the theoretical number of coulombs required to consume the starting phenol and are probably only accurate to ±15%. Reverse-phase liquid chromatography was performed on a 4.6 × 250 mm column of C-18 on 5 m silica having a pore size of 100 Å using UV detection.

4-Hydroxy-4-(2-vinyl-4,5-dimethoxyphenyl)-2,5-cyclohexadienone (5). To a solution of 2-bromo-4,5-dimethoxystyrene[4a] (2.35 g, 9.7 mmol) in THF (30 mL) at −78 °C was added *n*-BuLi (7.0 mL of a 1.45 M solution) dropwise. After being stirred for 2 h, a solution of 4-methoxy-4-(*tert*-butyldimethylsiloxy)-2,5-cyclohexadienone[5] (2.5 g) in THF (10 mL) was added dropwise, and the resulting mixture was stirred for 1 h at −78 °C and then allowed to warm to rt over 1 h. After the reaction was quenched by addition of saturated NH_4Cl (50 mL), extractive workup with Et_2O (150 mL) gave an oil which was dissolved in THF (150 mL) and treated with *n*-Bu_4NF (4.0 g) at 0 °C. After 30 min the reaction mixture was poured into cold brine (150 mL). The residue obtained from extractive workup with Et_2O (200 mL) was chromatographed on silica gel (6 in. × $^1/_2$ in. column, 1:1 EtOAc/PE as eluant) to afford **5** (0.66 g, 25% overall) as a white solid, mp 154−158 °C. Recrystallization of a portion from Et_2O/PE gave the analytical sample: mp 157−159 °C; IR (KBr) 1660 (s) cm^{-1}; ^1H NMR (80 MHz) δ 7.23 (s, 1 H), 6.58 (AB q, $\Delta\nu = 58$ Hz, $J = 10$ Hz, 4 H), 7.25−6.90 (m, X component of ABX, partially obscured, 1 H), 6.92 (s, 1 H), 5.4 (dd, A component of ABX, $J = 17$ Hz, 1H), 5.15 (dd, B component of ABX, $J = 11$ Hz, 1 H), 3.88 (s, 6 H), 2.34 (s, 1 H); HRMS calcd for $C_{16}H_{16}O_4$ m/z 272.1049, obsd 272.1058.

4-(2-Vinyl-4,5-dimethoxyphenyl)phenol (6a). To a solution of **5** (0.5 g, 1.8 mmol) in THF (5 mL) was added zinc−copper couple (0.25 g), and the resulting slurry was heated to reflux with vigorous stirring. Next, 5% HOAc (5 mL) was added dropwise over 5 min, and the mixture was heated and stirred for an additional 10 min. After cooling and addition of 5% HCl (25 mL), extractive workup with Et_2O (25 mL) gave **6a** (0.39 g, 83%) as a white solid, mp 127−131 °C. Recrystallization of a portion from Et_2O/PE gave the analytically pure material: mp 130−132 °C; IR (KBr) 3460 (m), 1610 (m), 1502 (s), 1270 (m), 1260 (m), 1235 (m), 1210 (m), 1198 (m), 1190 (m), 1135 (m) cm^{-1}; ^1H NMR (80 MHz) δ 7.10 (s, 1 H), 7.0 (AB q, $\Delta\nu = 27$ Hz, $J_{AB} = 8$ Hz, 4 H), 6.8−6.48 (m, X component of ABX, partially obscured, 1 H), 6.73 (s, 1 H), 5.53 (dd, A component of ABX, $J = 17$ Hz, 1 H), 5.06 (dd, B component of ABX, $J_{BX} = 11$ Hz, 1H), 4.8 (br s, 1 H), 3.93 (s, 3 H), 3.86 (s, 3 H); HRMS calcd for $C_{16}H_{16}O_3$ m/z 256.1100, obsd 256.1091; HRMS calcd for $C_{12}H_{17}O_3Br$ m/z 290.0341, calcd 290.0341.

4-(2-(2-Methyl-2-methoxyethyl)-4,5-dimethoxyphenyl)phenol (8). To a solution of **7** (1.5 g, 5.2 mmol) in THF (25 mL) at −78 °C was added *n*-BuLi (3.8 mL of 1.45 M solution) dropwise over 10 min, and the resulting mixture was stirred for 2 h at this temperature. Next, a solution of 4,4-dimethoxy-2,5-cyclohexadienone[20] (0.721 mL) in THF (10 mL) was added dropwise, and the mixture was stirred at −78 °C for 1 h and then allowed to warm to rt over 12 h. After the reaction was quenched by addition of saturated NH_4Cl (5 mL), extractive workup with Et_2O (75 mL) gave the crude product. This material was dissolved in $(CH_3)_2CO$ (100 mL), 5% HOAc (30 mL) was added, and the mixture was allowed to stand at room temperature. After 5 min TLC (1:1 Et_2O/PE) indicated the hydrolysis was complete. After addition of saturated $NaHCO_3$ (50 mL), extractive workup with $CHCl_3$ (3 × 25 mL) afforded the crude quinol. This material was dissolved in THF (10 mL) and was added to a suspension of zinc−copper couple (0.75 g) in 5% HOAc (8 mL). The resulting mixture was then stirred and heated at reflux for 1 h. After cooling, the mixture was poured into 5% HCl (25 mL) and diluted with Et_2O (100 mL). Workup afforded **8** (1.45 g, 92%) as an off-white solid, mp 145−150 °C, suitable for use in the next step. Recrystallization of a portion from Et_2O/PE gave white crystals: mp 153.5−155 °C; IR (KBr) 3211 (m), 1502 (m), 1362 (m), 1222 (m), 1195 (m), 1168 (m), 1052 (m), 1030 (m) cm^{-1}; ^1H NMR (80 MHz) δ 7.15 (s, 1 H), 6.96 (AB q, $\Delta\nu = 26$ Hz, $J = 9$ Hz, 4 H), 6.56 (s, 1 H), 5.0 (s, 1 H), 3.93 (s, 3 H), 3.82 (s, 3 H), 3.06 (s, 3 H), 1.3 (s, 6 H); HRMS calcd for $C_{18}H_{22}O_4$ m/z 302.1518, obsd 302.1491.

4-(2-(2-Propenyl-4,5-dimethoxyphenyl))phenol (9a). A solution of **8** (1.25 g, 4.1 mmol) in acetic anhydride (50 mL) was heated at reflux for 1 h. The excess acetic anhydride was then removed in vacuo, and the residue was crystallized from Et_2O/PE to afford in two crops the acetate of **8** (0.944 g, 64%) as a white solid, mp 130−134 °C. Repeated recrystallization from Et_2O/PE gave the analytical sample: mp 137−139 °C; IR (KBr) 1755 (m), 1502 (s), 1336 (m), 1258 (m), 1242 (s), 1219 (s), 1200 (s), 1171 (s), 1080 (m), 1030 (m) cm^{-1}; ^1H NMR (80 MHz) δ 7.14 (AB q, $\Delta\nu = 18$ Hz, $J = 9$ Hz, 4 H), 7.13 (s, 1 H), 6.56 (s, 1 H), 3.91 (s, 3 H), 3.80 (s, 3 H), 3.02 (s, 3H), 2.31 (s, 3 H), 1.27 (s, 6 H); HRMS calcd for m/z $C_{20}H_{24}O_5$ 344.1624, obsd 344.1595.

To a solution of the acetate of **8** (0.675 g, 1.96 mmol) in $CHCl_3$ (335 mL) was added *p*-TsOH (35 mg), and the resulting mixture was heated at reflux for 15 min, after which time TLC (2:1 Et_2O/PE) indicated complete reaction. Extractive workup gave the olefin (0.567 g, 93%) as a white solid, mp 95−99 °C, suitable for use in the next step. Recrystallization of a portion from Et_2O/PE gave white crystals: mp 101−103 °C; IR (KBr) 1770 (m), 1601 (m), 1520 (m), 1500 (s), 1462 (m), 1370 (m), 1340 (m), 1200 (br, s), 1130 (m), 750 (m) cm^{-1}; ^1H NMR (80 MHz) δ 7.22 (AB q, $\Delta\nu = 27$ Hz, $J = 9$ Hz, 4 H), 6.79 (s, 2 H), 5.0 (str m, 2 H), 3.90 (s, 3 H), 3.87 (s, 3 H), 2.30 (s, 3 H), 1.66 (br s, 3 H); HRMS calcd for $C_{19}H_{20}O_4$ m/z 312.1361, obsd 312.1361.

A solution of the product from above (0.56 g, 1.8 mmol) in CH_3OH (50 mL) containing 1% by weight KOH was stirred at rt for 15 min after which time TLC (2:1 Et_2O/PE) indicated completion of the reaction. Removal of the CH_3OH in vacuo and extractive workup with Et_2O (3 × 25 mL) afforded a brown oil which was dissolved in a minimum of Et_2O/PE and allowed to crystallize. The product was collected by vacuum filtration and air dried to afford **9a** (0.396 g, 81%) as a white, crystalline solid, mp 109−111 °C. Recrystallization of a portion from Et_2O/PE gave the analytically pure material as white needles: mp 110−111 °C; IR (KBr) 1505 (s) cm^{-1}; ^1H NMR (80 MHz) δ 7.05 (AB q, $\Delta\nu = 37$ Hz, $J = 9$ Hz, with both components partially obscured, 4 H), 6.78 (m, 2 H), 5.0 (str m, 2 H), 4.65 (s, 1 H), 3.92 (s, 3 H), 3.89 (s, 3 H), 1.66 (br s, 3 H); HRMS calcd for $C_{17}H_{18}O_3$ m/z 270.1256, obsd 270.1234.

1-Hydroxy-1-(2-propenyl)-4,4-(ethylenedioxy)-2,5-cyclohexadiene. A solution of benzoquinone monoethylene ketal[21] (5.00 g, 32.9 mmol) in THF (60 mL) was cooled to 0 °C, and 2-propenylmagnesium bromide (83 mmol) was added slowly via syringe. After all of the Grignard had been added, the ice bath was removed, and the mixture was stirred for 1 h. After addition of saturated NH_4Cl (15 mL) and removal of

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[20] Swenton, J. S.; Bradin, D.; Gates, B. D. *J. Org. Chem.* **1991**, *56*, 6156.

[21] Biggs, T. N.; Swenton, J. S. *J. Org. Chem.* **1992**, *57*, 5568.

the THF *in vacuo*, Et_2O (60 mL) was added, and the resultant slurry was filtered through Celite. Extractive workup with Et_2O (3 × 80 mL) gave a dark orange oil (6.05 g). The oil was chromatographed on base-washed silica gel[11] [5 × 1 in. column, 20% Et_2O/PE (300 mL), 50% Et_2O/PE (400 mL) as eluants] to yield a white crystalline alcohol (2.70 g, 42%): mp 88−89 °C; IR (KBr) 3467 (s), 2962 (m), 2888 (m), 1412 (s), 1379 (m), 1207 (m), 1138 (s), 1115 (s), 1080 (m), 1069 (m), 1015 (s), 992 (m), 956 (s), 911 (m) cm^{-1}; ^1H NMR δ 5.90 (s, 4 H), 5.32 (br s, 1 H), 5.0 (br s, 1 H), 4.09 (s, 4 H), 1.70 (br s, 3 H); HRMS calcd for $C_{11}H_{14}O_3$ m/z 194.0943, obsd 194.0920.

4-Methoxy-4-(2-propenyl)-2,5-cyclohexadienone (11). To a slurry of NaH (0.272 g, 11.3 mmol) in THF (50 mL) was added (2.00 g, 10.3 mmol) of the above alcohol dissolved in THF (30 mL). The reaction mixture was heated at reflux for 1 h and then cooled to rt. Methyl iodide (1.93 mL) was added, and the system was stirred for an additional 1 h after which time TLC (50% Et_2O/PE) indicated that no starting material remained. The reaction was quenched by addition of H_2O (25 mL), and extractive workup with Et_2O (3 × 40 mL) gave 2.50 g of the ether which was carried on crude to the next step.

To the crude product dissolved in THF (50 mL) was added 5% HCl (15 mL), and the reaction mixture was stirred for 24 h at rt. The reaction was quenched by addition of saturated $NaHCO_3$ (15 mL), and extractive workup with Et_2O (3 × 30 mL) gave a yellow solid which was recrystallized form cold hexane to afford white crystals of **11** (0.696 g, 41% yield): mp 47−48 °C; IR (KBr) 3270 (m), 2995 (m), 2945 (m), 1675 (s), 1637 (m), 1604 (s), 1454 (m), 1390 (m), 1085 (s), 912 (m), 855 (s) cm^{-1}; ^1H NMR δ 6.69 (d, J = 10.4 Hz, 2 H), 6.38 (d, J = 10.4 Hz, 2 H), 5.36 (s, 1 H), 5.08 (s, 1 H), 3.30 (s, 3 H), 1.69 (br s, 3 H); HRMS calcd for $C_{10}H_{12}O_2$ m/z 164.0837, obsd 164.0860.

4-Methoxy-4-(2-propenyl)-5-(*p*-(*tert*-butyldimethylsiloxy)phenyl)-2-cyclohexenone (14). Trimethylaluminum (10 mL, 2.0 M) was added slowly, accompanied by evolution of a large volume of methane gas, to a solution of BHT (8.8 g, 40 mmol) and CH_2Cl_2 (115 mL). After methane gas evolution ceased, the MAD solution was cooled to −78 °C, and (0.690 g, 4.2 mmol) of **11** dissolved in CH_2Cl_2 (5 mL) was added, resulting in a dark red/brown complex solution. After 15 min, (4-(*tert*-butyldimethylsiloxy)phenyl)magnesium bromide (10.5 mL, 1.2 M in CH_2Cl_2) was added to the MAD complex solution, resulting in a lightening of the intensely colored solution. The reaction mixture was stirred for 0.5 h, the reaction was quenched by addition of CH_3OH (5 mL) and H_2O (15 mL), and then the reaction mixture was allowed to warm to rt. The resultant slurry of aluminum and magnesium salts was filtered through Celite. After concentration of the filtrate *in vacuo*, extractive workup with CH_2Cl_2 (3 × 30 mL) and chromatography of the residue on silica gel [6 in. × 0.5 in. column, 100% PE (150 mL); 5% Et_2O/PE (100 mL); 10% Et_2O/PE (100 mL); 15% Et_2O/PE (100 mL) as eluant] gave two fractions as slightly yellow oils: 0.469 g of pure product and 0.977 g with a slight impurity. The 0.977 g fraction was rechromatographed on silica gel (3 in. × 0.5 in. column, 5% Et_2O/PE) as eluant) to give pure **14** (0.857 g), overall yield (84%), mp 73−74 °C: IR (KBr) 2956 (s), 2930 (s), 2892 (m), 2860 (m), 1691 (s), 1609 (m), 1514 (s), 1472 (m), 1465 (m), 1390 (m), 1258 (s), 1172 (m), 1093 (s), 1062 (m), 909 (s), 848 (s), 840 (s), 823 (m), 799 (m), 779 (s) cm^{-1}; ^1H NMR (80 MHz) δ 7.07 (d, J = 8 Hz, 2H), 7.02 (d, J = 10.2 Hz, 1 H), 6.72 (d, J = 8 Hz, 2 H), 6.24 (d, J = 10.2 Hz, 1 H), 5.00 (d, J = 1 Hz, 1 H), 4.73 (s, 1 H), 3.21 (3 line m, 5 H), 2.50 (m, 1 H), 1.42 (s, 3 H), 0.97 (s, 9 H), 0.18 (s, 6 H); HRMS calcd for $C_{22}H_{32}O_3Si$ m/z 372.2122, obsd 372.2124.

4-[5-Methoxy-2-(2-propenyl)phenyl]phenol (9c). The above ketone (600 mg, 1.63 mmol), CH_3OH (120 mL), trimethyl orthoformate (30 mL), and *p*-TsOH (60 mg) were heated at reflux for 12 h, after which time no starting ketone remained. The reaction was quenched by addition of $NaHCO_3$ (30 mL), and the CH_3OH was removed *in vacuo*. Extractive workup with Et_2O (3 × 60 mL) gave an oil. This residue was then dissolved in CH_3OH (10 mL) and added to a solution formed from Na (35 mg) and CH_3OH (95 mL). The reaction mixture was heated at reflux for 1.25 h, and then the reaction was quenched by adding saturated NH_4Cl (30 mL). Extractive workup with Et_2O (3 × 60 mL) and silica gel chromatography [5 in. × 0.25 in. column, 100% CH_2Cl_2 as eluant] gave **9c** as a slightly yellow oil (376 mg, 97%): IR (NaCl) 3390 (m, br), 1610 (s), 1518 (s), 1490 (m), 1467 (m), 1442 (m), 1371 (m), 1317 (m), 1295 (m), 1254 (m), 1220 (s), 1210 (s), 1173 (s), 1039 (m), 892 (m), 833 (s), 811 (m), 785 (m), 758 (m), 610 (m), cm^{-1}; ^1H NMR δ 7.4−7.2 (complex m, 3 H), 6.9−6.8 (m, 4 H), 5.10 (s, 1 H), 5.03 (s, 1 H), 4.96 (s, 1 H), 3.84 (s, 3 H), 1.64 (s, 3 H); HRMS calcd for $C_{16}H_{16}O_2$ m/z 240.1151, obsd 240.1166.

Anodic Oxidation of 9d. A solution of **9d** (0.25 g, 0.92 mmol) in 4:1 CH_3CN/CH_3OH (150 mL) containing HOAc (0.28 mL) and 1% by weight $LiClO_4$ as the electrolyte was anodically oxidized at 0 °C in a single cell with perforated cylindrical platinum sheet anode and copper wire cathode at a constant current of 0.05 A for 60 min (92% current efficiency) until no starting material remained by TLC (2:1 Et_2O/PE). After addition of a saturated $NaHCO_3$ solution (50 mL), extractive workup gave **17d** (0.255 g, 92%) as a light yellow powder, mp 143−146 °C. Recrystallization of a portion of this material from Et_2O/PE gave the analytical sample: mp 145.5−147 °C; IR (KBr) 1660 (s), 1501 (s), 1460 (m), 1445 (m), 1290 (m), 1280 (m), 1219 (m), 1065 (m), 850 (m) cm^{-1}; ^1H NMR (80 MHz) δ 7.15−6.13 (highly str m, 4 H), 6.83 (s, 1 H), 6.37 (s, 1 H), 3.90 (s, 3 H), 3.78 (s, 3 H), 3.18 (s, 3 H), 2.42 (AB q, $\Delta\nu$ = 28 Hz, J = 14 Hz, 2 H), 1.64 (s, 3 H); HRMS calcd for $C_{18}H_{20}O_4$ m/z 300.1361, obsd 300.1344. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.66. Found: C, 71.89; H, 6.76.

General Procedure for Iodobenzene Diacetate Oxidation. A general procedure for iodobenzene diacetate oxidation can be described as follows. To a solution of the 4-(2′-alkenylphenyl)phenol (0.5 mmol) in CH_3OH (40 mL) at 0 °C were added iodobenzene diacetate (209 mg, 0.65 mmol) and NaOAc (100 mg, 2.4 equiv). The resulting suspension was stirred for 5−10 min, poured into H_2O (30 mL), and concentrated *in vacuo*. The residue was extracted with EtOAc (3 × 20 mL), and the combined organic layer was washed with brine (50 mL) and dried through $CaSO_4$. The crude product was purified via silica gel chromatography (0.2 × 12 in., 3−15% EtOAc/PE as eluants) to afford the pure products. The spectral data for the products not reported in the anodic oxidations section are given in the supporting information.

4-(2-Acetylphenyl)phenol. To a solution of 3′-methoxy-3′-methyl-3′*H*-spirocyclohexa-2,5-diene-1-isobenzofuran-4-one[17a] (0.5 g, 2.0 mmol) in THF (2.5 mL) was added zinc-copper couple (0.24 g), and the resulting mixture was heated at reflux for 30 min and then cooled to rt. After addition of cold 5% HCl (25 mL) extractive workup with Et_2O (2 × 25 mL)) gave a light yellow oil which crystallized to give 4-(2-acetylphenyl)-phenol (0.41 g, 96%, mp 115−118 °C). Recrystallization from Et_2O/PE gave analytically pure material: mp 118−119 °C; IR (KBr) 1685 cm^{-1}; ^1H NMR (200 MHz) δ 7.6−7.45 (str m, 2 H), 7.45−7.3 (str m, 2 H), 7.04 (AB q, $\Delta\nu$ = 62 Hz, J = 9 Hz, 4 H), 2.08 (s, 3 H), OH absorption not detected; HRMS calcd for $C_{14}H_{12}O_2$ m/z 212.0837, obsd 212.0819.

4-[2-(1-(Phenylthio)vinyl)phenyl]phenol (25). To a 0° solution of the 4-(2-acetylphenyl)phenol (1.07 g, 5.05 mmol) under Ar in THF (90 mL) was added $TiCl_4$ (10.1 mmol, as a 1 M solution in CH_2Cl_2) dropwise with rapid stirring.[22] The resulting red solution was allowed to warm to rt followed by dropwise addition of a THF solution (20 mL) of thiophenol (0.725 mL, 7.07 mmol) and triethylamine (2.11 mL, 15.2 mmol). The reaction mixture was stirred for 15 min followed by addition of 5% HCl (30 mL). Extractive workup with Et_2O (2 × 20 mL) gave a yellow oil which was purified by silica gel chromatography [2 × 20 cm column, PE (200 mL), 8% EtOAc/PE (500 mL) as eluants] to give the vinyl sulfide **25** as a clear colorless oil (1.21 g, 79%): IR (neat) 3396 (br), 1516, 1476, 1256, 748 cm^{-1}; ^1H NMR (C_6D_6) δ 7.5−7.4 (m, 1 H), 7.4−7.25 (m, 2 H), 7.38 (d, J = 4 Hz, overlapping with m at ca. 7.3, 2 H), 7.25−7.18 (m, 1 H), 7.10−7.0 (m, 2 H), 6.85−6.45 (m, 3 H), 6.63 (d, J = 7 Hz, 2 H), 5.11 (s, 1 H), 4.48 (s, 1 H), 4.39 (s, 1 H); HRMS calcd for $C_{20}H_{16}OS$ m/z 304.0922, obsd 304.0924.

Anodic Oxidation of 25. A 0 °C solution of the vinyl sulfide **25** (0.2 g, 0.65 mmol) in $CH_3CN/HOAc/CH_3O$ (8:1:1)

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(22) Mukaiyama, T.; Saigo, K. *Tetrahedron Lett.* **1973**, 479.

(100 mL) containing $LiClO_4$ (0.50 g) was anodically oxidized at 50 mA for 1.25 h. The dark solution was then neutralized with saturated $NaHCO_3$ (20 mL) followed by addition of solid $NaHCO_3$. The solution was filtered and concentrated in vacuo. Extractive workup with Et_2O (40 mL) gave an oily tan solid which was chromatographed on Florisil [2 × 15 cm column, PE (200 mL), 5% EtOAc/PE (100 mL), 10% EtOAc (250 mL) as eluants] to give the dione **26** (0.058 g, 72%) identical with the known compound.[17a]

Acknowledgment. We thank the National Science Foundation for partial support of this work and the Honors College at OSU for an undergraduate research scholarship to Mr. Jeff Rohde.

Supporting Information Available: All experimental procedures not listed in the body of the paper and all ^1H NMR spectra of compounds reported in the paper (71 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering.

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