Anodic Oxidation of Phenolic Compounds. 4.[1a] Scope and Mechanism of the Anodic Intramolecular Coupling of Phenolic Diarylalkanes

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Abstract: Anodic oxidation in acetonitrile of a series of diarylalkanes (**1**–**13**) substituted with a phenol ether group (E) at one end and a phenolic group (P) at the other end was investigated. High yields of spirodienones (**14**–**19**) can always be obtained from the diarylpropanes when E is 3,4-dimethoxyphenyl (**1**–**6**). This anodic cyclization reaction follows three mechanistic pathways: electrophilic attack by the cation radical product from the ether moiety on the unoxidized phenolic part, intramolecular coupling between the cation radical product from the ether moiety and the radical product from the phenolic moiety, or electrophilic attack by the phenoxonium ion product from the phenolic moiety on the unoxidized ether part. When E is 3-methoxyphenyl, high yields of spirodienones are obtained only if the 3 and 5 positions of the phenolic part are blocked (**8**). The cyclization then follows the phenoxonium ion pathway. When E is 3,4,5-trimethoxyphenyl, the product is a polymer obtained via the cation radical of the ether part. Diarylethanes or -butanes did not cyclize on anodic oxidation. Oxidation of the compounds (**1**–**13**) using thallium tris(trifluoroacetate) (TTFA) was also investigated. The diarylethanes and -butanes gave no cyclization products with this reagent, but all the diarylpropanes (**1**–**9**) gave high yields of the corresponding spirodienones (**14**–**24**). The high selectivity of TTFA appears to be due to initial formation of a thallium phenolate.

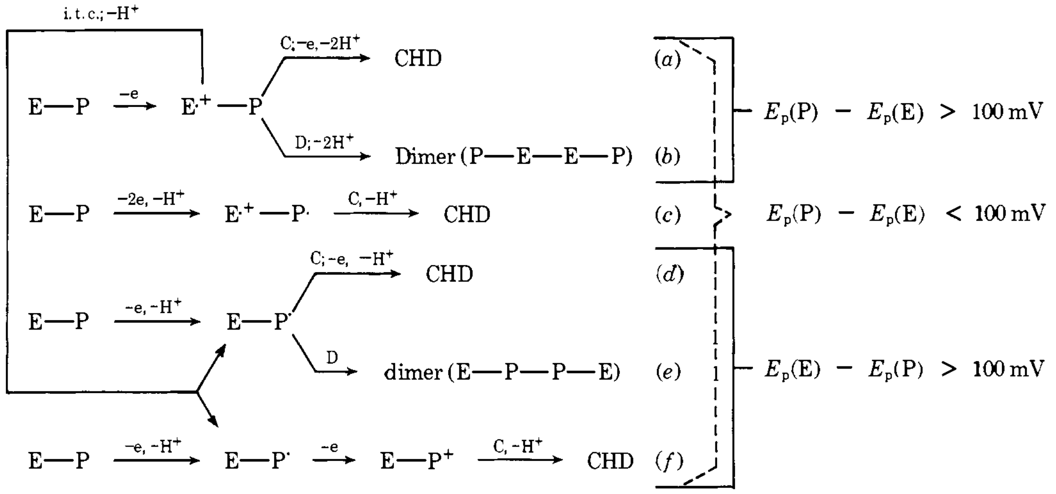
In a previous communication[2] we demonstrated that 1-(4-hydroxyphenyl)-3-(3,4-dimethoxyphenyl)propane (**4**) and 1-(4-hydroxyphenyl)-3-(3,4-methylenedioxyphenyl)propane (**5**) on anodic oxidation give the spirodienones **17** and **18** in high yield.[3] We suggested that these spirodienones were formed by an initial two-electron oxidation and deprotonation of the phenolic part of the diarylpropane giving a phenoxonium ion, followed by cyclization by an electrophilic attack of the phenoxonium ion on the unoxidized phenol ether part (f in Scheme I).

In view of the great biosynthetic importance and preparative utility of this coupling reaction, we have now investigated the anodic oxidation of a series of diarylalkanes (**1**–**13**) in order to establish the generality of the reaction and to get a better understanding of the mechanism involved. For comparison we have also studied the analogous chemical oxidation of **1**–**13** with thallium tris(trifluoroacetate) (TTFA). TTFA has recently[4] been shown to be a very efficient reagent for the intramolecular coupling of phenolic diarylpropanes to spirodienones.

Results

Cyclic voltammetry in acetonitrile or methylene chloride was found to be a very efficient diagnostic tool for determining the course of the anodic oxidation of these diarylalkanes (**1**–**13**). In general two anodic peaks are observed: a completely irreversible peak (A) and a quasireversible peak (B) at higher potential. Compounds whose cyclic voltammograms did not change through a series of consecutive sweeps invariably gave very high yields of spirodienones in the preparative anodic oxidations (compounds **1**, **2**, **6**, and **8**). When the peak heights in the cyclic voltammograms diminished slowly through a series of consecutive sweeps, high yields of spirodienones could still be obtained, but the results of preparative anodic oxidations varied greatly with changes in experimental conditions (compounds **3**, **4**, and

Scheme I[a]



[a] Possible mechanisms for the anodic oxidation of phenolic diarylalkanes (1–13); E = phenol ether part and P = phenolic part of the diarylalkane (E–P); $E\cdot^+$ = cation radical product from the phenol ether part; P· = the phenoxy radical product from the phenolic part; P^+ = the cation product (phenoxonium ion) from the phenolic part; CHD = spirodienone; C = cyclization; D = dimerization; i.t.c. = intramolecular charge transfer.

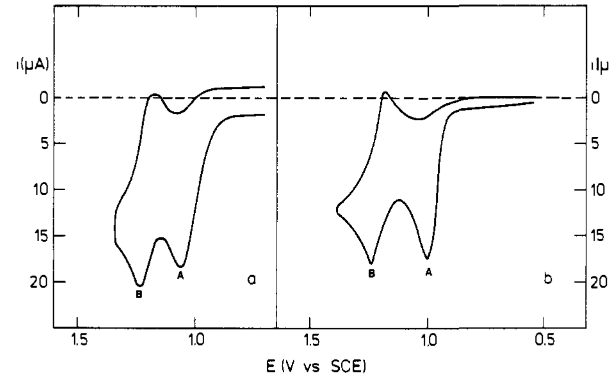
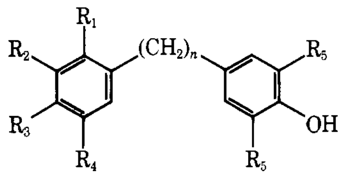


Figure 1. Cyclic voltammograms for the oxidation of a 1 mM solution of compound **2** in (a) acetonitrile containing lithium perchlorate (0.1 M) at 20 °C and (b) in CH_2Cl_2-TFMS (1%) containing n-Bu_4NBF_4 (0.1 M) at −50 °C; sweep rate, 100 mV/s. Potentials referred to the saturated calomel electrode.

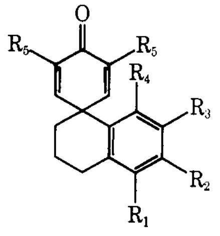
Table I. Half-Peak Potentials ($E_{p/2}$) for Compounds 1–13 Determined from Their Cyclic Voltammograms[a]

Substrate	$E_{p/2}$(A), V	$E_{p/2}$(B), V
1[b]	0.74	1.25
2[b]	0.99	1.16
3[c]	0.99	1.14
4[c]	1.09	1.21
5[c]	1.13	1.26
6[b]	1.13	1.20
7	1.14	*e*
8[b]	1.15	1.42
9	1.21	*e*
10[d]	1.11	1.20
11	1.24	*e*
12	1.13	*e*
13	1.16	*e*

[a] Measured at 20 °C in a 1 mM solution of the substrate in acetonitrile [methylene chloride containing tetrabutylammonium tetrafluoroborate (n-Bu_4NBF_4, 0.1 M) gives the same results] containing lithium perchlorate (0.1 M). The measuring electrode was a platinum button (diameter 0.5 mm) melted into a glass rod (diameter 5 mm) with a planar end. The reference was a saturated aqueous calomel electrode; the counter electrode was a platinum wire; voltage sweep rate, 100 mV/s. [b] The voltammograms did not change through a series of consecutive cycles. [c] The peak heights diminish gradually through a series of consecutive cycles. [d] The anode became passivated after the first cycle. [e] The anode became passivated in the first sweep past E_p(A), and measurements above this potential could not be made.



1, n = 3; R_1, R_4 = H; R_2, R_3, R_5 = OMe
2, n = 3; R_1, R_4 = H; R_2, R_3 = OMe; R_5 = Me
3, n = 3; R_1 = Me; R_3, R_4 = OMe; R_2, R_5 = H
4, n = 3; R_1, R_4, R_5 = H; R_2, R_3 = OMe
5, n = 3; R_1, R_4, R_5 = H; R_2, R_3 = $-OCH_2O-$
6, n = 3; R_1, R_4 = H; R_2, R_3 = OMe; R_5 = t-Bu
7, n = 3; R_1, R_5 = H; R_2, R_3, R_4 = OMe
8, n = 3; R_1, R_2, R_3 = H; R_4 = OMe; R_5 = t-Bu
9, n = 3; R_1, R_2, R_3, R_5 = H; R_4 = OMe
10, n = 2; R_1, R_2, R_5 = H; R_3, R_4 = OMe
11, n = 2; R_1, R_2, R_3, R_5 = H; R_4 = OMe
12, n = 4; R_1, R_2, R_5 = H; R_3, R_4 = OMe
13, n = 4; R_1, R_2, R_3, R_5 = H; R_4 = OMe



14, R_1, R_4 = H; R_2, R_3, R_5 = OMe
15, R_1, R_4 = H; R_2, R_3 = OMe; R_5 = Me
16, R_1 = Me; R_2, R_5 = H; R_3, R_4 = OMe
17, R_1, R_4, R_5 = H; R_2, R_3 = OMe
18, R_1, R_4, R_5 = H; R_2, R_3 = $-OCH_2O-$
19, R_1, R_4 = H; R_2, R_3 = OMe; R_5 = t-Bu
20, R_1, R_5 = H; R_2, R_3, R_4 = OMe
21, R_1, R_3, R_4 = H; R_2 = OMe; R_5 = t-Bu
22, R_1, R_2, R_3 = H; R_4 = OMe; R_5 = t-Bu
23, R_1, R_3, R_4, R_5 = H; R_2 = OMe
24, R_1, R_2, R_3, R_5 = H; R_4 = OMe

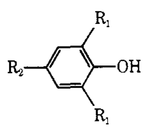
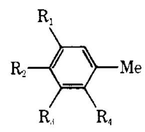
5). When severe filming (passivation) of the working electrode occurred already in the first anodic sweep, the preparative oxidations gave only polymers (compounds **7** and **10**–**13**). The half-peak potentials ($E_{p/2}$) determined from the cyclic voltammograms of compounds **1**–**13** are given in Table I, and a typical voltammogram is shown in Figure 1.

In order to determine the number of electrons (n) transferred in the oxidation at E_p(A), a series of coulometric oxidations were carried out on compounds **1**–**6** and **8** (due to anode passivation no meaningful n values could be obtained for the other compounds in Table I). All compounds gave n values in the range 1.9–2.1. During the coulometric oxidation, cyclic voltammograms were recorded at regular intervals; in all cases the height of peak A decreased linearly with time, but the height of peak B remained unchanged. At the end of each coulometric experiment, an authentic sample of the corresponding spirodienone (prepared by TTFA oxidation of the phenol under investigation) was added. In every case this gave an increase in peak B. From this we conclude that peak B corresponds to oxidation of a spirodienone formed by the oxidation of peak A.

The $E_{p/2}$ values determined from the cyclic voltammograms of the simple phenols and phenol ethers **25**–**33** are given in Table II. If the oxidation potentials of the aryl groups in compounds **1**–**13** are not affected by the presence of the second aryl group, the $E_{p/2}$ values in Table II should make it possible to determine if one or both of the aryl groups are involved in the oxidation taking place at E_p(A).

Recently we have shown[5] that the deprotonation of a number of phenol cation radicals to the corresponding phenoxy radicals is sufficiently slow at −50 °C in methylene chloride containing 1% of fluorosulfuric acid (with this concentration of FSO_3H, very little protonation of the phenol occurs) to allow measurement of the reversible redox potential for the reaction: phenol $\underset{+e}{\overset{-e}{\rightleftharpoons}}$ phenol cation radical. It was found that these reversible redox potentials were generally about 300 mV more anodic than the irreversible peak potentials (Tables I and II) measured at 20 °C in acetonitrile (or methylene chloride) and that the difference between the reversible redox potentials (measured at −50 °C in CH_2Cl_2-FSO_3H) for a phenol and the corresponding methyl ether is less than 100 mV[6] These findings indicated that further insight into the mechanism of the anodic cyclization of phenolic diarylalkanes could be obtained from a voltametric study in CH_2Cl_2-FSO_3H at −50 °C. However, FSO_3H is a powerful sulfonating reagent toward aromatic compounds, and for that reason solvent systems containing FSO_3H are not suitable for preparative anodic oxidations of such compounds. For example, about 90% of the substrate or the product were lost through sulfonation in preparative anodic oxidation experiments with compounds **4** and **5** in

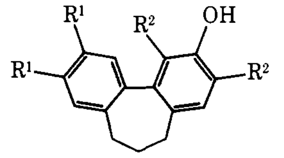
Table II. Half-Peak Potentials ($E_{p/2}$) of Simple Phenols and Phenol Ethers Determined from Their Cyclic Voltammograms[a]

 	$E_{p/2}$, V	 	$E_{p/2}$, V
25, R_1 = OMe; R_2 = Me	0.85	**29**, R_1, R_2, R_3 = OMe; R_4 = H	1.11
26, R_1 = Me; R_2 = Et	1.10	**30**, R_1, R_2 = —O—CH_2—O—; R_3, R_4 = H	1.17
27, R_1 = *t*-Bu; R_2 = Me	1.23	**31**, R_1, R_2 = OMe; R_3, R_4 = H	1.19
28, R_1 = H; R_2 = Me	1.27	**32**, R_1, R_2 = OMe; R_3 = H; R_4 = Et	1.32
		33, R_1 = OMe; R_2, R_3, R_4 = H	1.54

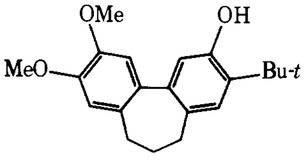
[a] Measured as described in note *a* in Table I.

CH_2Cl_2-FSO_3H (1%) at −50 °C. We therefore investigated a series of sulfonic acids in order to find a nonsulfonating substitute for FSO_3H. It turned out that trifluoromethanesulfonic acid (TFMS) affected the voltammetry of simple phenols in exactly the same way as FSO_3H[5] without causing sulfonation. Hence, TFMS was used instead of FSO_3H in the present study. The voltammograms obtained for compounds **2** and **4–6** in CH_2Cl_2-TFMS (1%) at −50 °C were very similar, and the only differences from voltammograms recorded in acetonitrile or methylene chloride were that peak A showed a slight (~50 mV) cathodic shift and became sharper and that the redox reaction occurring at peak B became reversible. The voltammograms for compound **2** are shown in Figure 1. By coulometry it was shown that for compounds **4** and **5**[7] the first, irreversible oxidation peak (A) corresponds to a two-electron oxidation and the second, reversible, peak (B) corresponds to a one-electron oxidation (these experiments were monitored by rotating-disk electrode voltammetry[8]). By addition to the voltammetry and coulometry solutions of the spirodienones **17** and **18** corresponding to the diarylalkanes **4** and **5**, it was established that the product formed at the potential of peak A is the spirodienone. This then undergoes a reversible one-electron oxidation to the cation radical at the potential of peak B.

The products **34a** and **34b**, formed by acid-catalyzed dienone-phenol rearrangement of the spirodienones **18** and **19**, are formed in about 95% yield from preparative anodic oxidations of **4** and **5** in CH_2Cl_2-TFMS at −50 °C. That rearranged products are observed in the preparative experiments but not in the voltametric or coulometric experiments is explained by the difference in time scale between these experiments. A typical preparative oxidation required 5–7 h, whereas a voltametric/coulometric experiment was finished within half an hour.



34a, R^1 = OMe; R^2 = H
34b, R^1 = $-OCH_2O-$; R^2 = H
34c, R^1 = OMe; R^2 = Me
34d, R^1 = R^2 = OMe



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Depending on the current density, *n* values between 2 and 3 were obtained from coulometric experiments with **2**. Preparative oxidation of **2** in CH_2Cl_2-TFMS at −50 °C gave (Table III) **34c** in 95% yield. Voltametry on the spirodienone **15** at −50 °C in CH_2Cl_2-TFMS (Figure 2) showed that it undergoes a reversible one-electron oxidation (O_2–R_2) and that it slowly ($k = 3 \times 10^{-3}\ s^{-1}$) rearranges to a new compound which undergoes two consecutive one-electron oxidations (O_1–R_1 and O_3–R_3). The height of the couples O_1–R_1 and O_3–R_3 increased on addition of **34c**, indicating that **15** rearranges to **34c**.

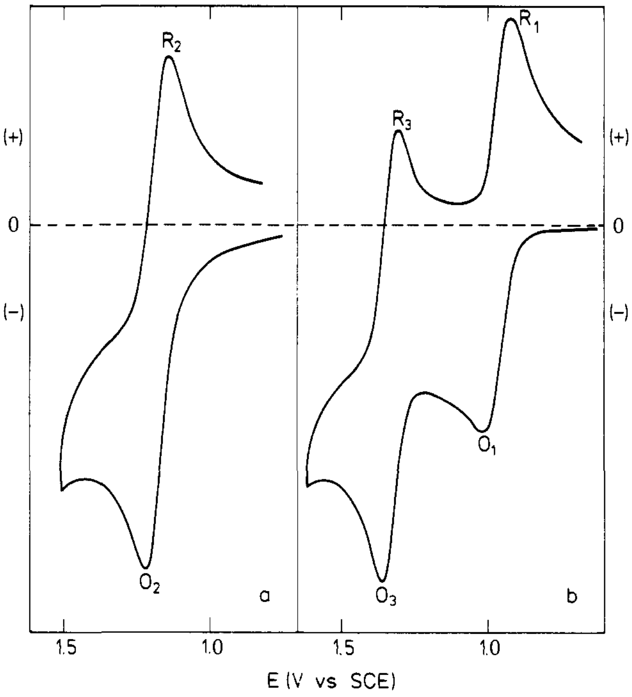


Figure 2. Cyclic voltammograms for the oxidation of a 1 mM solution of compound **15** in CH_2Cl_2–TFMS (1%) containing *n*-Bu_4NBF_4 (0.1 M) at −50 °C. (a) Voltammogram recorded 2 s after the addition of TFMS and (b) 15 min after; sweep rate, 100 mV/s. Potentials referred to the saturated calomel electrode.

The voltammetry of compound **3** in CH_2Cl_2-TFMS at −50 °C gave results completely different (Figure 3) from those obtained in pure methylene chloride or acetonitrile. In methylene chloride the voltammetry is similar to that of compounds **2** and **4–6**. However, on addition of TFMS (1%), peak A becomes reversible and now involves the transfer of only one electron (coulometry and comparison with peak height for compound **34c**), while the second peak becomes completely irreversible. A preparative anodic oxidation experiment in CH_2Cl_2-TFMS at −50 °C gave no cyclized products. The NMR spectrum of the product indicated that oxidation of the 1-methyl group in the phenol ether moiety had occurred with formation of a benzyl alcohol derivative (after hydrolytic workup).

Preparative Electrolyses. The results of preparative electrolyses and of the oxidations with TTFA are given in Table III. The same results were obtained with acetonitrile/lithium perchlorate or CH_2Cl_2/*n*-Bu_4NBF_4; however, since the workup was much easier with CH_3CN/Me_4NBF_4 as electrolysis medium, this was preferred. In the first electrolysis experiments, the yields of spirodienones from **3**, **4**, **5**, and **9**

Table III. Preparative Anodic Oxidations and TTFA Oxidations of the Diarylalkanes 1–13

	Anodic oxidations					
	Acetonitrile[a]		CH_2Cl_2–TFMS[b]		TTFA oxidations[c]	
Substrate	Conversion (%)[d]	Products, yield (%)[e]	Conversion (%)[d]	Products, yield (%)[e]	Conversion (%)[d]	Products, yield (%)[e]
1	85	**14** (85)	100	**34d** (89)	85	**14** (80)
2	75	**15** (80)	98	**34c** (94)	80	**15** (90)
3	86	**16** (80)	86	Unidentified	75	**16** (85)
4	80	**17** (75)	99	**34a** (93)	95	**17** (95)
5	75	**18** (80)	98	**34b** (96)	95	**18** (95)
6	75	**19** (80)	100	**35** (60)	60	**19** (90)
7	*f*	Polymers[g]	28	Polymers[g]	95	**20** (80)
8	70	**21** (80)	30	Polymers[j]	45[h]	**21** (75); **22** (15)
9	*f*	Polymers,[i] **23** (40)	24	Polymers[j]	85	**23** (60); **24** (40)
10	*f*	Polymers	92	**52** (87)	0	
11	*f*	Polymers	19	Polymers[j]	0	
12	*f*	Polymers	87	**53** (81)	0	
13	*f*	Polymers	21	Polymers[j]	0	

[a] Carried out on a 0.02 M solution of the substrate in acetonitrile containing tetramethylammonium tetrafluoroborate (0.01 M). The anode was platinum, and the potential was kept constant = $E_{p/2}$(A). The amount of current passed through the cell was 2 F/mol in all experiments. [b] Carried out on a 0.02 M solution of the substrate in methylene chloride containing tetrabutylammonium tetrafluoroborate (0.05 M) and TFMS (0.1 M) at −50 °C with constant current (10 mA). The amount of current passed through the cell was 2 F/mol in all experiments. [c] Carried out as described for compound 5 in ref 4. One mole of TTFA per mole of substrate was used in all experiments. [d] Amount of starting material consumed and equal to the current efficiency if a two-electron oxidation is assumed. [e] These yields are based on consumed starting material. The yields based on the total amount of starting material are obtained by multiplication of conversion and yield given in the table. [f] The anode rapidly became passivated due to formation of a polymeric film. The same results were obtained using a graphite or carbon felt anode. In order to get 2 F/mol of current through the cell, the anode had to be reactivated by heating in an open flame at regular intervals. In such experiments, the conversion was still only about 20%. [g] These polymers were assigned structure 36 on the basis of their NMR spectra. [h] If 2 mol of TTFA were used the conversion was 75% and the yield of 22 and 23 was 90% (the ortho–para ratio did not change). [i] These polymers were assigned structure 37 on the basis of their NMR spectra. [j] In these polymers, coupling has occurred both in the ether and in the phenolic moieties (NMR).

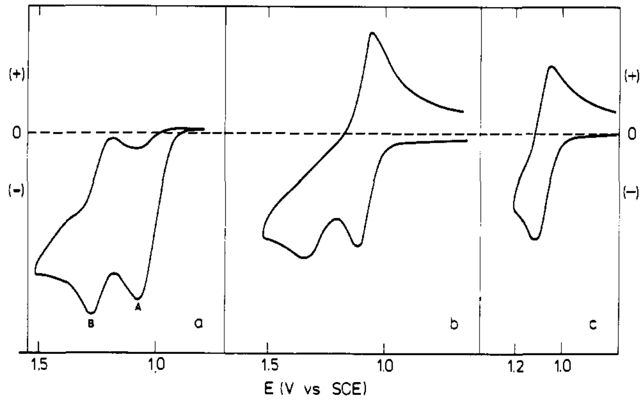


Figure 3. Cyclic voltammograms for the oxidation of a 1 mM solution of compound 3 in (a) methylene chloride containing n-Bu_4NBF_4 (0.1 M) at −50 °C, (b) and (c) in CH_2Cl_2–TFMS (1%) at −50 °C; sweep rate, 100 mV/s. Potentials referred to the saturated calomel electrode.

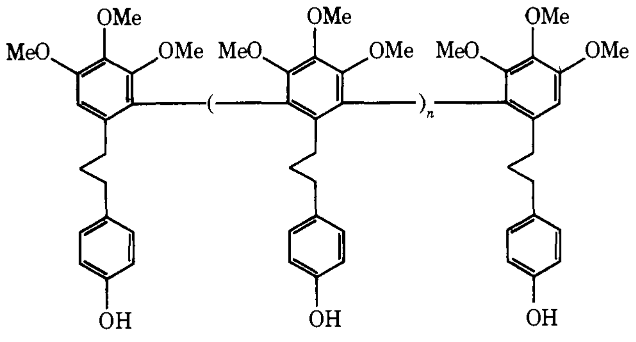
were very variable, and passivation of the anode through polymer formation usually occurred. With **1**, **2**, and **8** no such problems were encountered. In order to find the reason for this, a series of experiments were carried out in which the effects of changing anode potential, temperature, concentration of starting material, supporting electrolyte, solvent, and anode material were studied. However, none of these changes affected the undesirable anode film formation. It turned out that the important variable was the stirring rate. With very slow stirring rates (see Experimental Section) and an anode potential equal to $E_{p/2}$(A), **16–18** could be obtained from **3–5** (Table III). However, the anodic cyclization of **9** to **23** reported previously[2] could not be repeated.

The diarylalkanes **10–13** did not afford any cyclized products on anodic oxidation in acetonitrile, methylene chloride, or trifluoroacetic acid[9] (TFA) or on oxidation with TTFA. These anodic oxidations gave only polymers and starting material, and the current efficiency (based on conversion to polymers **36**) was very low due to passivation of the anode. However, anodic oxidation of **10** or **12** in CH_2Cl_2–TFMS at −50 °C at low potential gave a dimer (**52** or **53**) with bond formation between the 6 positions of the 3,4-dimethoxyphenyl groups. The structures of the dimers were determined by methylation with dimethyl sulfate and comparison of the resulting phenol ethers with authentic samples prepared previously.[9,15] In the oxidations of **10–13** with TTFA, starting material was recovered almost quantitatively after hydrolytic workup regardless of the reaction time.

In our preliminary communication[2] we reported the formation of compounds **38** and **39** during anodic oxidation of **5** and **6**. These were believed to be formed by a reduction-rearrangement reaction of the spirodienones **17** and **18** at the cathode. In the present study we have deliberately employed a cathode with a much larger surface area, and the only reaction at the cathode was the reduction of protons formed at the anode (undivided cell). We attempted to hinder cathodic reaction of the spirodienones by separating anode and cathode chambers with an ion-exchange membrane. However due to the decreasing pH of the anolyte during electrolysis, extensive acid-catalyzed rearrangement of the spirodienones occurred. This could be avoided by buffering the anolyte with solid sodium carbonate. The yields of spirodienones thus obtained were similar to those given in Table III. A large cathode area in an undivided cell is thus, in the present systems, equivalent to working in a divided cell with a buffered anolyte.

Discussion

The products obtained by anodic oxidation of the diarylalkanes **1–13** in acetonitrile (Table III) or in CH_2Cl_2–TFMS could in principle be formed via one or more of six different mechanistic pathways (a–f, Scheme I). In Scheme I we have considered two-electron oxidations only. We have assumed *that* there is no electronic interaction between the



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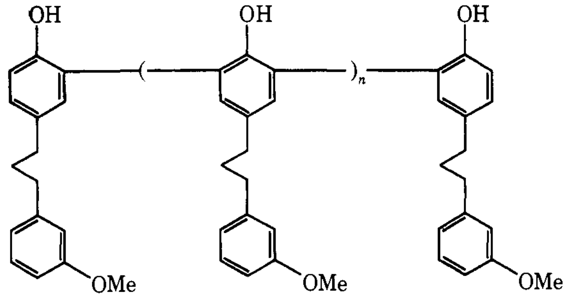

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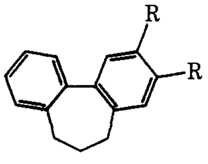
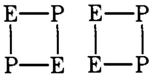


38, R = OMe
39, R, R = $-OCH_2O-$

phenolic moiety (P) and the phenol ether moiety (E) of the diarylalkane (E—P); *that* the cation radicals formed by oxidation of either the phenol ether part ($E\cdot^+$—P) or the phenolic part (E—$P\cdot^+$) are not oxidized to the dications (E^{2+}—P or E—P^{2+}), thus further oxidation of these cation radicals should occur in the unoxidized aryl group with formation of a dication diradical ($E\cdot^+$—$P\cdot^+$)[10]; *that* the preferred reaction of a phenol cation radical is deprotonation, i.e., cyclization of intermediates where the phenolic part is oxidized to the cation radical (E—$P\cdot^+$ or $E\cdot^+$—$P\cdot^+$) does not occur;[11] *that* the preferred reaction of the intermediate $E\cdot^+$—P· where both aryl groups have lost an electron is cyclization since no products derived from dimerization (viz. **40**) or polymerization (viz. **41**) of this species were encountered; *that* intermediates containing the phenol ether part as a free radical (E·—P or E·—P·) need not be considered here since deprotonation of $E\cdot^+$ to E· would involve cleavage of a carbon hydrogen bond with the formation of a highly energetic sp^2-hybridized radical.[12]



$$\begin{array}{ccc} E\text{—}P & & E\text{—}P \\ | \quad | & & | \quad | \\ P\text{—}E & & E\text{—}P \end{array}$$

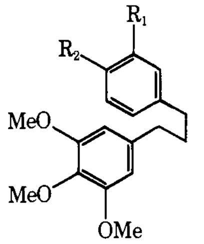
40

$$E\text{—}P(\text{—}P\text{—}E\text{—})_n E\text{—}P \qquad E\text{—}P(\text{—}E\text{—}P\text{—})_n P\text{—}E$$

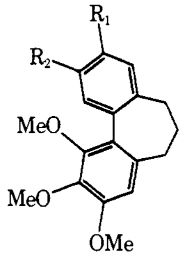
41

The various reaction paths possible (Scheme I) have been divided into three groups.

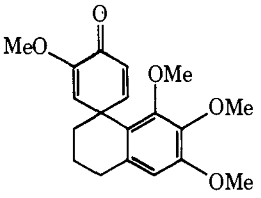
(I) **$E_p(P) - E_p(E) > 100$ mV.** Disregarding differences in charge-transfer rates, adsorption, solvation, etc. between the phenolic and the phenol ether parts of the diarylalkanes **1–13**, this difference between the oxidation (peak) potentials should allow selective (>95%) oxidation of the phenol ether moiety.[13] From Tables I and II it follows that only compound **7** falls in this category. On anodic oxidation (Table III) **7** yields only polymer of structure **36** with bond formation exclusively between trimethoxyphenyl rings. Similarly the diarylpropanes **42** and **43** on anodic oxidation in acetonitrile (platinum anode) also yield polymers with bond formation between trimethoxyphenyl rings.[14] This indicates that only mechanism b is operating. It is somewhat surprising that no cyclized product is formed on anodic oxidation of **7** (or **42–43**), since we have found in a previous study[15] that cyclization of the diarylpropane **44** via a mechanism similar to (a) giving either the spirodienone **17** (high oxidation potential) or the rearranged product **45** (low potential) is a very favorable reaction[16] (Scheme II). This reversal of the relative rates of cyclization (a) and dimerization (b) on going from **4** to **7** (or **44** to **42**) can be explained by lower electrophilicity (due to more efficient delocalization of the positive charge) of the cation radical derived from the trimethoxyphenyl group relative to that of the cation radical of the 3,4-dimethoxyphenyl group. Further, the more efficient charge delocalization should diminish the electrostatic repulsion between the cation radicals of **7**, and this would favor the dimerization reaction but not the cyclization. In accordance with this interpretation, the cyclized product **49** is obtained in quantitative yield by anodic oxidation of **46** in acetonitrile.[14] Here the nucleophilicity of the aryl ring which does not undergo oxidation is increased by addition of a further methoxy group. The compounds **47**[14] and **48**[14,17] also give quantitative yields of cyclized products (**50** and **51**). However, in these cases the phenolic moiety is oxidized more easily than the phenol ether moiety by 150 mV, and the reactions probably follow pathway f.



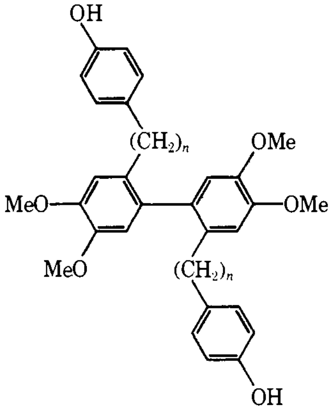
42, R_1 = H; R_2 = OMe
43, R_1 = OMe; R_2 = H
46, R_1, R_2 = OMe
47, R_1 = OH; R_2 = OMe
48, R_1 = OMe; R_2 = OH



49, R_1, R_2 = OMe
50, R_1 = OH; R_2 = OMe



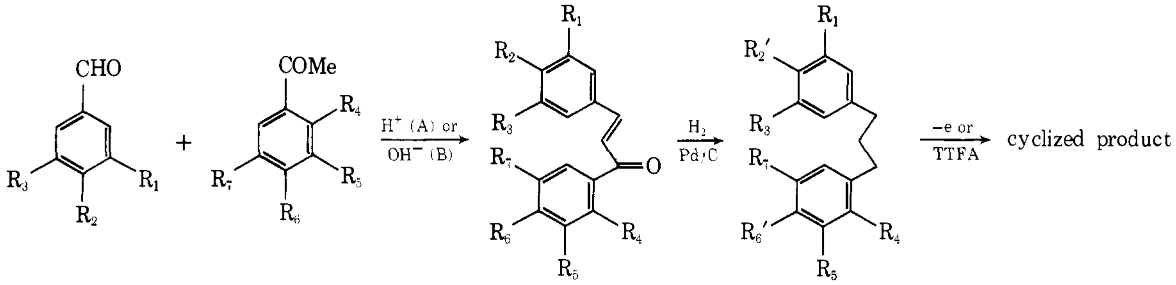
51



52, $n = 2$
53, $n = 4$

(II) **$E_p(E) - E_p(P) > 100$ mV.** Here selective oxidation of the phenolic part should be possible. Compounds **1**, **8**, and **9** fall in this category. Table III shows that **1** and **8** on anodic oxidation yield spirodienones (**14** and **19**) exclusively, while

Table IV. Synthesis of the Diarylpropanes 1–9. Characterization of the Cyclization Products from Anodic and TTFA Oxidation of Compounds 1–9



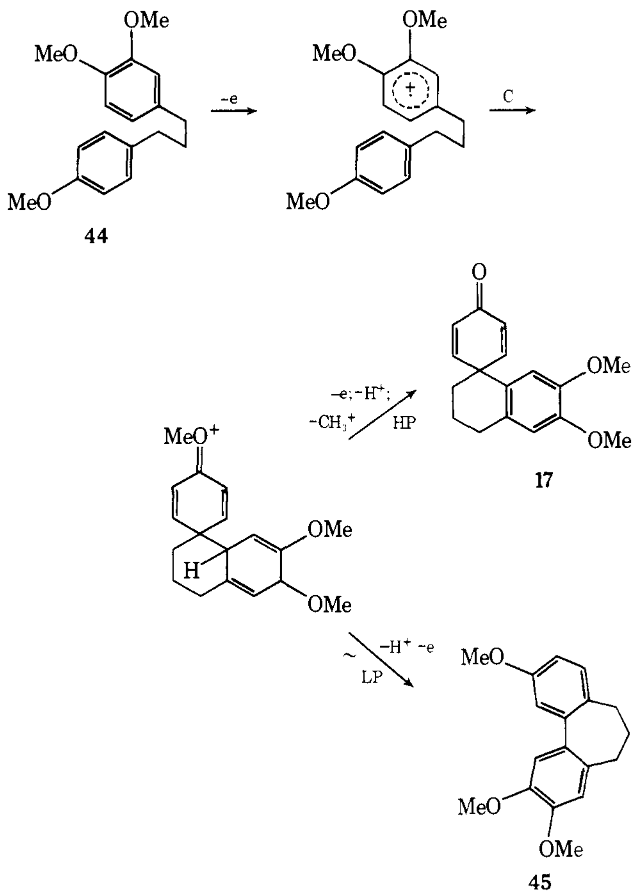
Benzaldehyde precursor[a]	Acetophenone precursor[b]	Method[c]	Diarylpropenone yield (%), mp (°C)	Diarylpropane;[d] mp (°C); NMR[e] (ppm); $M^+(m/e)$	Cyclized product;[f] mp (°C); NMR (ppm); $M^+(m/e)$
R_1, R_3 = OMe; R_2 = OBz	R_4, R_5 = H; R_6, R_7 = OMe	B	81, 99–101	1; 72–74; 3.87 (s, 12 H), 6.40 (s, 2 H), 6.73 (m, 3 H); 332	**14**; 147–148; 2.00 (m, 4 H), 2.86 (m, 2 H), 3.67 (s, 6 H), 3.87 (s, 3 H), 6.12 (s, 2 H), 6.43 (s, 1 H), 6.68 (s, 1 H); 330
R_1, R_2 = OMe; R_3 = H	R_4 = H; R_5, R_7 = Me; R_6 = OH	A	56, 191–193	2; 121–122; 2.22 (s, 6 H), 3.87 (s, 6 H), 6.73 (m, 5 H); 300	**15**; 99–100; 1.92 (m, 4 H), 2.82 (m, 2 H), 3.70 (s, 3 H), 3.85 (s, 3 H), 6.33 (s, 1 H), 6.60 (s, 1 H), 6.77 (s, 2 H); 298 34c; glass; 2.25 (s, 3 H), 2.28 (s, 3 H), 2.30 (m, 6 H), 3.85 (s, 3 H), 3.93 (s, 3 H), 5.00 (s, 1 H), 6.80 (s, 2 H), 6.88 (s, 1 H); 298
R_1, R_3 = H; R_2 = OBz	R_4 = Me; R_5 = H; R_6, R_7 = OMe	B	81; 176–177.5	3; 84–88; 2.18 (s, 3 H), 3.83 (s, 6 H), 6.90 (m, 6 H); 286	**16**; 101–103; 1.87 (m, 4 H), 2.23 (s, 3 H), 2.66 (m, 2 H), 3.60 (s, 3 H), 3.81 (s, 3 H), 6.32 (d, *J* = 10 Hz, 2 H), 6.78 (s, 1 H), 7.08 (d, *J* = 10 Hz, 2 H); 284
R_1, R_2 = OMe; R_3 = H	R_4, R_5, R_7 = H; R_6 = OBz	B	84; 129–130	4; 79–81; 3.87 (s, 6 H), 6.87 (m, 7 H); 272	17; 95–96[g]; 1.95 (m, 4 H), 2.87 (m, 2 H), 3.73 (s, 3 H), 3.90 (s, 3 H), 6.30 (d, *J* = 10 Hz, 2 H), 6.43 (s, 1 H), 6.67 (s, 1 H), 6.83 (d, *J* = 10 Hz, 2 H); 270 34a;[h] 202–206; 2.32 (m, 6 H), 3.90 (s, 3 H), 3.97 (s, 3 H), 4.98 (s, 1 H), 6.78 (m, 5 H); 270
R_1, R_2 = O—CH_2—O; R_3 = H	R_4, R_5, R_7 = H; R_6 = OBz	B	83; 147–148	5; 74–76; 5.90 (s, 2 H), 6.85 (m, 7 H); 256	18; 169–171,[i] 1.92 (m, 4 H), 2.80 (m, 2 H), 5.87 (s, 2 H), 6.25 (d, *J* = 10 Hz, 2 H), 6.42 (s, 1 H), 6.62 (s, 1 H), 7.03 (d, *J* = 10 Hz, 2 H); 254 34b;[h] 198–201; 2.33 (m, 6 H), 4.95 (s, 1 H), 5.88 (s, 2 H), 6.80 (m, 5 H); 245

Table IV (*Continued*)

Benzaldehyde precursor[a]	Acetophenone precursor[b]	Method[c]	Diarylpropenone yield (%), mp (°C)	Diarylpropane;[d] mp (°C); NMR[e] (ppm); $M^+(m/e)$	Cyclized product;[f] mp (°C); NMR (ppm); $M^+(m/e)$
R_1, R_3 = *t*-Bu; R_2 = OH	R_4, R_7 = H; R_5, R_6 = OMe	A	76; 153–155	**6**; 74–75.5; 1.45 (s, 18 H), 3.87 (s, 6 H), 6.76 (s, 2 H), 6.92 (m, 3 H); 384	**19**; 134–136; 1.27 (s, 18 H), 1.95 (m, 4 H), 2.86 (m, 2 H), 3.70 (s, 3 H), 3.89 (s, 3 H), 6.37 (s, 1 H), 6.73 (s, 2 H); 382 **35**; 212–214; 1.45 (s, 9 H), 2.40 (s, 6 H), 3.87 (s, 3 H), 3.92 (s, 3 H), 4.98 (s, 1 H), 6.70 (s, 1 H), 6.80 (s, 1 H), 6.90 (s, 1 H), 7.12 (s, 1 H); 326
R_1, R_2, R_3 = OMe	R_4, R_5, R_7 = H; R_6 = OBz	B	77; 142–144	**7**; 91–93; 3.80 (s, 9 H), 6.37 (s, 2 H), 6.87 (m, 4 H); 302	**20**; 154–156; 1.87 (m, 4 H), 2.85 (m, 2 H), 3.67 (s, 3 H), 3.78 (s, 3 H), 3.87 (s, 3 H), 6.27 (d, *J* = 10 Hz, 2 H), 6.47 (s, 1 H), 7.03 (d, *J* = 10 Hz, 2 H); 300
R_1, R_3 = *t*-Bu; R_2 = OH	R_4, R_6, R_7 = H; R_5 = OMe	A	68; 143–145.5	**8**; oil; 1.45 (s, 18 H), 3.77 (s, 3 H), 6.92 (m, 6 H); 354	**21**; 148–150; 1.26 (s, 18 H), 1.90 (m, 4 H), 2.88 (m, 2 H), 3.77 (s, 3 H), 6.67 (m, 5 H); 352 **22**;[j] oil; 1.26 (s, 18 H), 1.85 (m, 4 H), 2.86 (m, 2 H), 3.53 (s, 3 H), 6.67 (m, 5 H); 352
R_1 = OMe; R_2, R_3 = H	R_4, R_5, R_7 = H; R_6 = OBz	B	77; 115–116.5	**9**; bp (0.01 mm) 165–170; 3.77 (s, 3 H), 6.97 (m, 8 H); 242	**23**; 170–173; 1.88 (m, 4 H), 2.87 (m, 2 H), 3.79 (s, 3 H), 6.23 (d, *J* = 10 Hz, 2 H), 6.70 (m, 3 H), 6.99 (d, *J* = 10 Hz, 2 H); 240 **24**;[j] 220–222; 1.95 (m, 4 H), 2.87 (m, 2 H), 3.60 (s, 3 H), 6.22 (d, *J* = 10 Hz, 2 H), 6.73 (m, 3 H), 6.97 (d, *J* = 10 Hz, 2 H); 240

[a] 3,5-Di-*tert*-Butyl-4-hydroxybenzaldehyde was prepared as described by M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1439 (1957); the other aldehydes were commercial. [b] 3,5-Dimethyl-4-hydroxyacetophenone was prepared by aluminum chloride catalyzed Fries rearrangement of 2,6-dimethylphenyl acetate (from acetylation of 2,6-xylenol); 1-methyl-3,5-dimethoxyacetophenone was prepared as described by C. W. Perry, M. V. Kalnins, and K. H. Deitcher, *J. Org. Chem.*, 37, 4371 (1972); the other acetophenones were commercial. [c] Procedure described in the text. [d] The hydrogenations were carried out in ethanol with a hydrogen pressure slightly above atmospheric (Pd/C, 10%, Merck; substrate:catalyst ratio = 10:1). The quality of the catalyst was found to be very important. Only the Merck catalyst was able to reduce the chalcones beyond the benzyl alcohol stage. The reduction time varied from 7 to 48 h. After the hydrogenation/benzyl ether cleavage, the catalyst was removed by filtration and the solvent by evaporation. The product thus obtained was pure diarylpropane. [d] If R_2 = OBz or OH then R_2' = OH and R_6' = R_6; if R_6 = OBz or OH then R_6' = OH and R_2' = R_2. [e] The NMR signals for the protons of the alkyl chain were the same for all diarylpropanes: a two-proton multiplet around 1.90 ppm and a four-proton multiplet around 2.57 ppm. Only NMR signals for the aromatic protons and for the protons in the substituents of the aromatic rings are given in the table. [f] For yields, see Table III. All the spirodienones exhibited a strong, characteristic absorption peak at 1665–1670 cm^{-1} in their ir spectra. [g] Lit. (ref 17) 95.5–96.5 °C. [h] Identified by methylation with dimethyl sulfate and comparison of the resulting methyl ether with an authentic sample prepared as described in ref 15. [i] Lit. (ref 4) 169–171 °C. [j] The structure was assigned on the basis of a comparison of the chemical shift of the methoxy group with the chemical shifts of the methoxy groups in compounds 16, 17, and **20**. It is seen that the chemical shift of a methoxy group ortho to the coupling position is around 3.60 ppm, whereas methoxy groups meta or para to the coupling position have chemical shifts around 3.85 or 3.75 ppm. In accordance with this, the chemical shift of the methoxy group is 3.77 ppm in compound **21** and 3.79 ppm in compound **23**.

Scheme II[a]



[a] C = cyclization; HP = high potential; LP = low potential.

9 gives polymers and only a trace of the spirodienone (23). The formation of these spirodienones could in principle occur via both pathway d and pathway f (Scheme I). However, phenoxy radicals are poor electrophiles[1a] and, furthermore, are more easily oxidized than the corresponding phenols. We therefore believe that the spirodienones **14**, **19**, and **23** are formed mainly via path f. The fact that polymers are formed on anodic oxidation of **9** shows that the dimerization reaction (e) competes with further oxidation (path f) when both ortho positions in the phenolic part of the diarylalkane are free (although the phenoxy radicals are more easily oxidized than the phenol itself, this is entirely reasonable since the dimerization reaction e is very fast[2]); but since even a monomolecular layer of the polymer formed in the dimerization reaction e completely passivates the anode, it is impossible to estimate the relative rates of reactions e and f (reaction f might be much faster than reaction e). In conclusion, it appears that an anode that either adsorbs or complexes phenoxy radicals thereby preventing the dimerization reaction e would be ideal for electrosynthesis of spirodienones from phenolic diarylalkanes (cf. ref 1a).

(III) $|E_p(E) - E_p(P)| < 100$ mV. The voltametry (Tables I and II) for the compounds which fall into this category (**2**–**6**) does not allow any firm mechanistic conclusions. Oxidation may occur via all pathways in Scheme I since the difference in oxidation potential between the phenolic part and the ether part is small. However, the voltametric measurements and the preparative electrolyses carried out on compounds **2**–**5** in CH_2Cl_2-TFMS at −50 °C clarify the picture somewhat. The effect of TFMS at low concentration (1%) is to increase the oxidation potential of the phenolic part of the diarylalkane without affecting the oxidation potential of the phenol ether part. The results obtained for compound **3** show clearly that the increase in the oxidation potential of the phenolic part in going from pure methylene chloride (or acetonitrile) to methylene chloride containing TFMS (1%) is sufficient to allow selective oxidation of the phenol ether moiety. We therefore conclude that in the presence of TFMS, the oxidative cyclization of **2**, **4**, and **5** (and of **10** and **12**) is thus completely analogous to that of the corresponding methyl ethers,[9,15] and formation of the spirodienones **15**, **17**, and **18** (and **19**; see note 7) via mechanism a is a definite possibility when the oxidations are carried out in pure acetonitrile. However, the formation of the spirodienone **16** in high yield on oxidation of **3** in acetonitrile (or methylene chloride), but not in CH_2Cl_2-TFMS,[18] shows that for this particular compound cyclization does not follow path a in acetonitrile or methylene chloride.[18] This leaves us with mechanisms c and f for the formation of **16**. Of these two reactions only f is expected to show dependence on the stirring rate, because with increasing stirring rates the diffusion layer becomes thinner, and the chance that the phenoxy radicals formed in reaction f leave the diffusion layer and undergo dimerization before further oxidation can take place becomes greater. Reaction c does not involve intermediates which can dimerize or undergo further oxidation before cyclization. This means that the thickness of the diffusion layer is without importance for cyclization reaction c. From these considerations it follows that slow stirring rates should favor the formation of spirodienones in oxidations following path f (as observed in the oxidations of compounds **2**–**5**) and that cyclization of **3** via mechanism f does take place. The present data do not allow a determination of the importance of mechanism c for the cyclization of **3** to **16**. If the cyclization of **3** follows path f (and c) in acetonitrile, the same must be true for compounds **2** and **6** since $E_p(E) - E_p(P)$ is more positive for these compounds than for compound **3** (Table II) and as one of the positions para to a methoxy group in the ether moiety is free in both **2** and **6** we expect mechanism c to be more important for these compounds than for compound **3**. For compounds **4** and **5** the ether moiety is actually more easily oxidized (~80 mV, Table II) than the phenolic part and cyclization probably occurs via paths a and c as well as via f (dependence on stirring rate). It is interesting to note that selective oxidation of the phenolic part in **4** and **5** does take place to some extent although the phenol ether part is about 80 mV more easily oxidized. Oxidations of **10** and **12** give a similar result. In solvents like methylene chloride, acetonitrile, or TFA, **10** and **12** gave only polymers with exclusive bond formation between the phenolic moieties. In contrast, the corresponding methyl ethers on oxidation at low potential in TFA-CH_2Cl_2 give a dimer in which the dimethoxyphenyl groups are coupled.[9,15] These findings indicate that the phenoxy radical E—P· also can be formed by indirect oxidation via intramolecular charge transfer from the oxidized ether part of the cation radical $E\cdot^+$—P to the unoxidized phenolic part followed by deprotonation.

Oxidations with TTFA. The results in Table III show that TTFA is generally a more efficient reagent than the platinum anode for oxidation of phenolic diarylalkanes to spirodienones. Furthermore, these results show that the TTFA oxidation is not a straightforward electron-transfer reaction since compound **7**, in which the phenol ether part has a lower oxidation potential than the phenolic part, yields a spirodienone (**20**) on oxidation with TTFA. Most likely the TTFA oxidation follows a pathway[4] involving initial formation of a thallium phenolate which undergoes an intramolecular oxidation-cyclization reaction with formation of a spirodienone (together with thallium(I) trifluoroacetate and trifluoroacetic acid). This mechanism explains why TTFA selectively oxidizes the phenolic part of a diarylpropane in which the phenol ether part has lower oxidation potential, why no complications due to formation of free phenoxy radicals occur in the TTFA oxidations, and why the diarylpropanes (**6** and **8**) in which the hydroxy group is surrounded by bulky *tert*-butyl groups give low conversion in the TTFA oxidations (Table III).

Surprisingly, the compounds **10–13** were not oxidized by TTFA. Probably a thallium phenolate is formed even with these compounds, but due to the unfavorable length of the alkyl chain (see ref 15), the energy of the transition state for the oxidation-cyclization reaction (Scheme I) is very high. Thus the reaction stops at the thallium phenolate stage, and after hydrolytic workup the starting phenol is recovered. Assuming that this explanation is correct, the oxidation-cyclization reaction in Scheme I must be concerted. That is, phenoxonium ions are not intermediates in TTFA oxidations (phenoxonium ions would react at least with starting material to give dimers or polymers).

Experimental Section

General procedures and apparatus used for voltammetry and coulometry and purification of solvents were conventional and have been described in previous papers.[9,14] The NMR spectra were recorded in deuteriochloroform with Me_4Si as internal reference. Ir spectra were recorded in KBr tablets (for solids) or on thin films (for liquids).

Preparative Electrolyses. General. Oxidations in Acetonitrile. The compound to be oxidized (1 mmol) was dissolved in acetonitrile (50 ml) containing Me_4NBF_4 (100 mg) in a closed, water-cooled (11 °C), one-compartment cell (diameter 40 mm) fitted with a platinum-foil anode (50 cm^2) and a nickel-spiral cathode (diameter 1 mm, length 300 mm). The cell content was stirred magnetically with a Teflon-coated stirring bar (diameter 6 mm, length 30 mm). Slow stirring indicates 50–100 rpm, rapid stirring 500–1000 rpm. All oxidations were carried out at a constant potential equal to $E_{p/2}(A)$ with a saturated aqueous calomel electrode as reference. At this potential the cell current remains fairly constant around 8–10 mA. Electrolysis was interrupted when an amount of current corresponding to 2 F/mol had passed through the cell. The electrolysis mixture was evaporated under reduced pressure, and the residue was triturated with dry ether (3 × 25 ml) to precipitate Me_4NBF_4. The combined ether extracts were evaporated, and the resulting product was analyzed by TLC and NMR with nitromethane added as internal analytical standard. The spirodienones were obtained in a pure state by recrystallization of the crude product from methanol.

Oxidations in CH_2Cl_2–TFMS. A solution of n-Bu_4NBF_4 (800 mg) in methylene chloride (50 ml) contained in the electrolysis cell described above was cooled to −50 °C. TFMS (0.5 ml) and the compound to be oxidized (1 mmol) were added to this solution. The oxidations were carried out with slow stirring and constant current (10 mA). When 2 F/mol of current had passed through the cell, the electrolysis was interrupted and the reaction mixture poured into 1 M aqueous bicarbonate (100 ml). The organic phase was washed twice with water and worked up as described for the runs in acetonitrile.

Synthesis of the Diarylpropanes 1–9. The diarylpropanes 1–**9** were prepared by catalytic hydrogenation of the corresponding diarylpropenones (chalcones) which were synthesized by acid-catalyzed[19] (procedure A) or base-catalyzed[20] (procedure B) condensation of appropriately substituted benzaldehyde and acetophenone derivatives. In the base-catalyzed condensations, the phenolic hydroxyl function was protected by a benzyl group.[21] The experimental data are collected in Table IV.

Acid-Catalyzed Condensations (Procedure A). The benzaldehyde derivative (0.1 mol), the acetophenone derivative (0.1 mol), methylene chloride (100 ml), concentrated sulfuric acid (1 ml), and molecular sieve (3A, 10 g) were stirred at room temperature for 24 h. The red-colored solution was then decanted into a separatory funnel and washed twice with water (75 ml), saturated bicarbonate solution (75 ml), and water (75 ml). The residue obtained after evaporation of the methylene chloride was purified by recrystallization from 1:1 toluene–petroleum ether (the chalcones containing *tert*-butyl groups) or acetic acid (the other chalcones obtained by procedure A).

Table V. Elemental Analytical Data for Compounds 1–**24**, 34a–d, and **35**

Compd	Calcd for $C_xH_yO_z$: C (%); H (%)	Found: C (%); H (%)
1	$C_{19}H_{24}O_5$: 68.7; 7.2	68.8; 7.2
2	$C_{19}H_{24}O_3$: 76.0; 8.0	75.9; 8.0
3	$C_{18}H_{20}O_3$: 76.1; 7.0	76.0; 7.0
4	$C_{17}H_{20}O_3$: 75.0; 7.4	75.0; 7.3
5	$C_{16}H_{16}O_3$: 75.0; 6.3	75.1; 6.3
6	$C_{25}H_{36}O_3$: 78.1; 9.4	78.1; 9.4
7	$C_{18}H_{22}O_4$: 71.5; 7.3	71.3; 7.4
8	$C_{24}H_{34}O_2$: 81.4; 9.6	81.2; 9.5
9	$C_{16}H_{18}O_2$: 79.3; 7.4	79.0; 7.5
10	$C_{16}H_{18}O_3$: 74.4; 7.0	74.3; 7.0
11	$C_{15}H_{16}O_2$: 78.9; 7.0	78.8; 7.0
12	$C_{18}H_{22}O_3$: 75.5; 7.7	75.5; 7.6
13	$C_{17}H_{20}O_2$: 79.7; 7.8	79.6; 7.7
14	$C_{19}H_{22}O_5$: 69.1; 6.7	69.0; 6.7
15	$C_{19}H_{22}O_3$: 76.5; 7.4	76.3; 7.3
16	$C_{18}H_{20}O_3$: 76.1; 7.0	75.9; 7.1
17	$C_{17}H_{18}O_3$: 75.6; 6.7	75.4; 6.8
18	$C_{16}H_{14}O_3$: 75.6; 5.5	75.4; 5.5
19	$C_{25}H_{34}O_3$: 78.5; 8.9	78.4; 9.1
20	$C_{18}H_{20}O_4$: 72.0; 6.7	71.8; 6.7
21	$C_{24}H_{32}O_2$: 81.8; 9.1	81.8; 9.1
22	$C_{24}H_{32}O_2$: 81.8; 9.1	81.7; 9.1
23	$C_{16}H_{16}O_2$: 80.0; 6.7	79.9; 6.7
24	$C_{16}H_{16}O_2$: 80.0; 6.7	79.8; 6.8
34a	$C_{17}H_{18}O_3$: 75.6; 6.7	75.7; 6.6
34b	$C_{16}H_{14}O_3$: 75.6; 5.5	75.5; 5.4
34c	$C_{19}H_{22}O_3$: 76.5; 7.4	75.3; 7.4
34d	$C_{19}H_{22}O_5$: 69.1; 6.7	69.0; 6.6
35	$C_{21}H_{26}O_3$: 77.3; 8.0	77.4; 7.8

Base-Catalyzed Condensations (Procedure B). The benzaldehyde derivative (0.1 mol) and the acetophenone derivative (0.1 mol) were dissolved in boiling ethanol (200 ml), and aqueous sodium hydroxide (6 N, 2 ml) was added slowly with stirring. Stirring was continued without heating for 1.5 h. During this time the chalcone crystallized from the solution. The reaction mixture was then heated to the boiling point again for 15 min, cooled in ice, and filtered. The compounds thus obtained gave pure diarylpropanes on catalytic hydrogenation.

Synthesis of the Diarylethanes 10 and 11. The diarylethanes were prepared by catalytic hydrogenation of the corresponding stilbenes prepared from p-benzyloxybenzaldehyde and 3-methoxy- or 3,4-dimethoxybenzyl bromide using a modified Wittig reaction.[9]

1-(3,4-Dimethoxyphenyl)-2-(4-hydroxyphenyl)ethane (**10**): mp 108–111 °C; NMR δ (ppm) 2.82 (s, 4 H), 3.81 (s, 3 H), 3.83 (s, 3 H), 6.83 (m, 7 H); M^+ 258 (m/e).

1-(3-Methoxyphenyl-2-(4-hydroxyphenyl)ethane (11): bp (0.01 mm) 145–150 °C; NMR δ (ppm) 2.78 (s, 4 H), 3.80 (s, 3 H), 6.81 (m, 8 H); M^+ 224 (m/e).

Synthesis of the Diarylbutanes 12 and 13. The diarylbutanes were prepared by Grignard reaction in tetrahydrofuran of 4-benzyloxybenzaldehyde and 3-(3-methoxyphenyl)propyl bromide and 3-(3,4-dimethoxyphenyl)propyl bromide, followed by catalytic hydrogenation and hydrogenolysis (vide supra). The 3-arylpropyl bromides were prepared from the corresponding cinnamic acids[22] by reduction with lithium aluminum hydride[23] and bromination with phosphorus tribromide.[24]

1-(4-Hydroxyphenyl)-4-(3,4-dimethoxyphenyl)butane (**12**): bp (0.1 mm) 210–220 °C; NMR δ (ppm) 1.56 (m, 4 H), 2.57 (m, 4 H), 3.50 (s, 6 H), 6.87 (m, 7 H); M^+ 286 (m/e).

1-(4-Hydroxyphenyl)-4-(3-methoxyphenyl)butane (13): bp (0.1 mm) 179–180 °C; NMR δ (ppm) 1.561.56 (m, 4 H), 2.57 (m, 4 H), 3.48 (s, 3 H), 6.95 (m, 8 H); M^+ 256 (m/e).

Elemental analytical data for compounds 1–**24**, **34a–d**, and **35** are given in Table V.

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References and Notes

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(2) U. Palmquist, A. Ronlán, and V. D. Parker, *Acta Chem. Scand., Ser. B*, **28**, 267 (1974).

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(6) E_{rev}(phenol) > E_{rev}(phenol ether) for phenols with not more than one *o*-alkyl substituent and E_{rev}(phenol) < E_{rev}(phenol ether) for 2,6-dialkylphenols.

(7) The diarylalkanes containing *tert*-butyl groups (**6** and **8**) looses one *tert*-butyl group in the presence of TFMS. Cyclic voltammograms run at various times after the preparation of a 1 mM solution of **6** in CH_2Cl_2–TFMS (1%) at −50 °C showed that the rate constant for this dealkylation is about 4×10^{-4} s^{-1} under these conditions. In a preparative oxidation of **6** in CH_2Cl_2–TFMS at −50 °C, compound **35** was obtained in 60% yield with 100% conversion (two stereoisomeric spirodienones should be obtained from the diarylpropane with one *tert*-butyl group. However the same product (**35**) is formed by dienone–phenol rearrangement of these spirodienones). From this we conclude that **35** is formed by cyclization of the mono-*tert*-butyl compound.

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(10) This appears a reasonable assumption since our measurements in CH_2Cl_2–FSO_3H (ref 5) have shown that the oxidation potential for the oxidation of a cation radical of a phenol or a phenol ether is at least 300–400 mV more anodic than the oxidation potential for the oxidation of the phenol or phenol ether to the cation radical. Preparative experiments (Table III) were carried out at the latter potential.

(11) In our preliminary communication (ref 2) we argued on the basis of the difference in oxidation potential between a phenol and its methyl ether that the initial one-electron transfer from a phenol to an anode with formation of a cation radical is generally followed by rapid deprotonation to a phenoxy radical which can dimerize (path e in Scheme I), react as an electrophile (path d), or become further oxidized to a phenoxonium ion (path f). Our finding (ref 5) that the reversible potential (in CH_2Cl_2–FSO_3H) for the redox reaction

$$\text{phenol} \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{phenol cation radical}$$

is about the same as for the reversible redox reaction (also in CH_2Cl_2–FSO_3H),

$$\text{phenol ether} \underset{+e}{\overset{-e}{\rightleftharpoons}} \text{phenol ether cation radical}$$

of the corresponding methyl ether supports this hypothesis.

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Dimer Formation during Reactions of Benzylic Halides with Lithium Naphthalene and Mechanisms of Dimer Formation from Reactions of Benzylic Halides with Benzylic Carbanions

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Abstract: Reactions of benzylic fluorides and chlorides with lithium naphthalene in THF have been found to give dimers in 61–79% yields. Competition experiments using equimolar benzhydryl and benzyl chlorides with lithium naphthalene produced three possible ethane dimers in the statistically expected ratio of 1:2:1. Diphenylmethyllithium competition experiments using an excess of equimolar benzhydryl and benzyl chlorides produced equal amounts of *sym*-tetraphenylethane (**1**) and 1,1,2-triphenylethane (**2**) in fast reactions. Conversely, equimolar benzhydryl and benzyl fluorides reacted slowly with diphenylmethyl carbanion to produce **2** and **1** in unequal amounts (2:1 = 1.92). The large difference in reaction rate between benzylic chlorides and fluorides in reactions with benzylic carbanions together with the failure of trityl and benzhydryl fluorides to react with trityl carbanion have led to the suggestion that benzylic fluorides do not react with benzylic carbanions by an electron-transfer mechanism to produce dimers via a geminate radical pair intermediate. The failure of competition experiments between lithium naphthalene and equimolar trityl and benzhydryl fluorides to form significant amounts of pentaphenylethane was interpreted as evidence against dimer formation through a radical coupling pathway. Comparison of benzylic halide–lithium naphthalene reactions with benzylic halide–benzylic carbanion reactions indicates that dimer formation in aromatic radical anion reactions proceeds through a carbanion intermediate but follows two different mechanisms depending upon which halide is reduced. Benzylic chlorides react with their counterpart carbanions to yield dimers rapidly via an electron-transfer mechanism having a geminate radical pair intermediate whereas fluorides appear to react slowly by a classical displacement mechanism.

The reactions of alkyl halides with alkali metal naphthalenes have been studied intensively during the past 10 years.[1-8] There is general agreement that this aromatic radical anion reduces the halide by dissociative electron transfer to produce an organic radical and a halide anion via eq 1.[10] The alkyl radicals appear in part as an alkylation product of naphthalene and as simple reduction products, RH, or alkyl dimers, R–R. Substantial efforts have been devoted