

## Anodic Oxidation of Phenolic Compounds. Part 5.<sup>1</sup> Anodic Methoxylation of Phenols. A Simple Synthesis of Quinones, Quinone Acetals, and 4-Methyl- $\alpha$ -methoxycyclohexa-2,5-dienones

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The products and yields obtained on anodic oxidation in methanol of a series of phenols (1a—h) have been investigated as a function of anode material, anode potential, methanol concentration, supporting electrolyte, temperature, and substituents. *ortho*- and *para*-Methoxylated and dimeric products were observed. However, experimental conditions were found which, in favourable cases, allow selective formation of *para*-methoxylated products (isolated as a *para*-dienone or *para*-benzoquinone), *ortho*-methoxylated products (isolated as an *ortho*-dienone or the Diels–Alder adduct of this dienone), or dimeric products. The methoxylated products are formed *via* nucleophilic attack of methanol on an anodically generated phenoxylium ion; the dimeric products are probably formed by dimerisation of anodically generated phenoxy radicals.

QUINONES (13), quinone acetals (8), and dienones [(2) and (4)] are of great interest both in themselves and as versatile synthetic precursors. In a previous publication<sup>2</sup> dealing with the anodic hydroxylation of phenols we described a simple synthesis of quinones and 4-alkyl-4-hydroxycyclohexa-2,5-dienones. In this paper we describe a systematic investigation of the anodic methoxylation of phenols and the use of this reaction for the synthesis of quinones, quinone hemiacetals, 4-alkyl-4-methoxycyclohexa-2,5-dienones, and 2-alkyl-2-methoxycyclohexa-3,5-dienones. A similar investigation of the oxidation with thallium(III) nitrate of a number of phenols in methanol solution has been published recently.<sup>3</sup>

<sup>1</sup> Part 4, U. Palmquist, A. Nilsson, V. D. Parker, and A. Ronlán, *J. Amer. Chem. Soc.* 1976, **98**, 2571.

<sup>2</sup> A. Nilsson, A. Ronlán, and V. D. Parker, *J.C.S. Perkin I*, 1973, 2337.

### RESULTS AND DISCUSSION

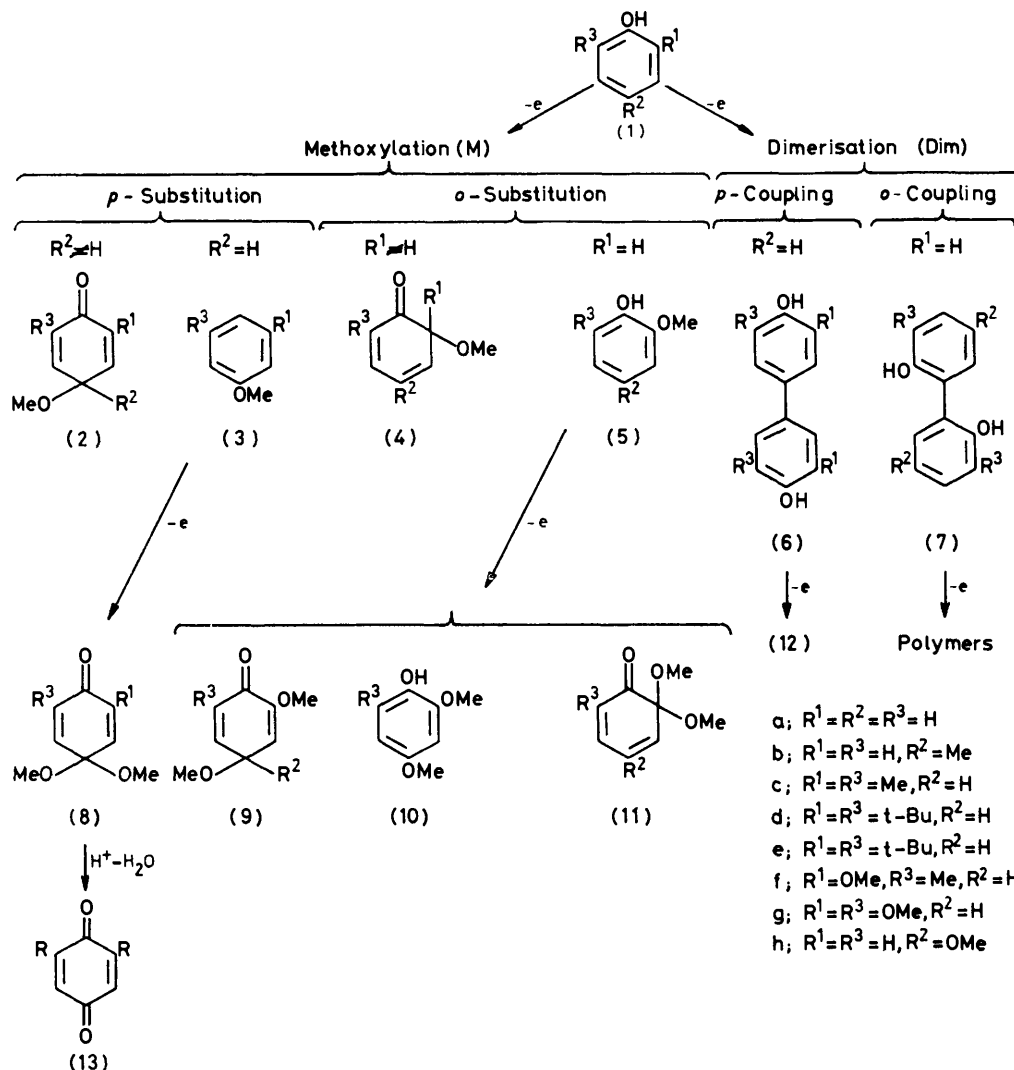
Phenol (1a), *p*-cresol (1b), 2,6-dimethylphenol (1c), 2,6-di-*t*-butylphenol (1d), 2,6-di-*t*-butyl-*p*-cresol (1e), 2-methoxy-4-methylphenol (1f), 2,6-dimethoxyphenol (1g), and 4-methoxyphenol (1h) were oxidised electrochemically in the presence of methanol. The types of products obtained are shown in Scheme 1. The compounds (9) and (11) were estimated only in the oxidations of (1b); the yields were small (4–10%).

In order to establish whether it is possible to achieve selective formation of *ortho*- or *para*-methoxylated or dimeric products, a series of experiments was carried out in which we investigated the effect of anode material, anode potential, methanol concentration, phenol concentration, supporting electrolyte, temperature, stirring

<sup>3</sup> A. McKillop, D. H. Perry, M. Edwards, S. Antus, L. Farkas, M. Nógrádi, and E. C. Taylor, *J. Org. Chem.*, 1976, **41**, 282.

rate, and phenol substituents on the ratio ( $p : o$ ) of the yields of *para*-methoxylated products ( $p$ ) and *ortho*-methoxylated products ( $o$ ) and the ratio [Dim : ( $p + o$ )]

most of the starting material consumed can be accounted for, indicating that the polymeric products are formed *via* an initial *ortho-ortho* or *ortho-para* coupling. The



SCHEME 1

of the yields of dimeric products (Dim) and methoxylated products ( $p + o$ ). The results are summarised in Tables 1 and 2. The phenols with unsubstituted *ortho*-positions [(1a), (1b), (1f), and (1h)] would be expected to give *ortho-ortho* or *ortho-para* coupled dimers [(7) in Scheme 1]. However no such products were isolated. This means that these products, if formed at all, must be destroyed by further oxidation. The fact that a large proportion of the starting material consumed in the oxidations of phenol (1a) and *p*-cresol (1b) is not accounted for shows that destructive oxidation does take place (with the formation of polymers and ultimately of carbon dioxide and water). In oxidations of phenols with both *ortho*-positions substituted [(1c), (1d), (1e), and (1g)],

*ortho*-methoxylated products [(5a), (5b), (5f), and (5h)] formed by oxidation of phenols (1a), (1b), (1f), and (1h) cannot be intermediates in the formation of polymers since they all give very high yields of further methoxylated products [e.g. (11)] on oxidation.<sup>4</sup> Furthermore the dienone (2b) (Scheme 1), and probably also the other dienones (4), (8), (9), and (11), on further oxidation gives products different from the polymers mentioned above.<sup>4</sup>

The results obtained on oxidation of phenol itself are noteworthy. When platinum is the anode material the main product is *p*-benzoquinone. However, when *p*-methoxyphenol is oxidised under similar conditions<sup>5</sup> the main product is 4,4-dimethoxycyclohexa-2,5-dienone (8a), indicating that *p*-benzoquinone is not formed *via*

<sup>4</sup> A. Nilsson and A. Ronl n, unpublished results (see also ref. 7).

<sup>5</sup> A. Nilsson, A. Ronl n, and V. D. Parker, *Tetrahedron Letters*, 1975, 1107.

*p*-methoxyphenol. When graphite is the anode material the main product from the oxidation of phenol in methanol is (8a). In benzene-methanol (1:1), oxidation of phenol on a graphite anode at a constant potential (2.0 V

(*p* + *o*) ratios in the conventional manner (see Table 3). Although the maximum possible error is very large, the actual error is probably considerably smaller since errors in the analytical procedure seldom all effect the final result

TABLE 1  
Anodic oxidation of phenols (1a—h) in methanol. Product pattern as a function of experimental conditions

[Phenol/M]	Experiment no.	[LiClO <sub>4</sub> ]/M	[NaHCO <sub>3</sub> ]/M	[Addend]/M	Anode	T(°C)	E/V	<i>b</i>	Q/F	mol <sup>-1</sup> e	Conversion (%)	<i>p</i> -Methoxylation ( <i>p</i> ,%)	<i>o</i> -Methoxylation ( <i>o</i> ,%)	Dimerisation (Dim,%)	Dim : ( <i>p</i> + <i>o</i> ) <i>p</i> : <i>o</i>
(1a) (0.15)	1	0.6	0.2		Pt	-60	2.5		4.5		100	37 <sup>h</sup>			
(1a) (0.11)	2	0.3	0.4		C <sup>i</sup>	10	2.0		6.8		100	46			
(1b) (0.15)	3	0.6	0.4		Pt	-60	2.1		2.0		55	20			
(1b)	4						2.5				59	33			
(1b)	5						2.7				48	31			
(1b)	6						2.5				61	17			
(1b) (0.05)	7	0.3	0.25		C <sup>i</sup>	10	2.0				62	35	10		3.5
(1b)	8						2.5				65	34	7		4.9
(1b)	9	0.6				-60	2.0				56	39	6		6.5
(1b)	10						2.5				18	33	4		8.3
(1b) (0.04)	11	0.3	0.2		PbO <sub>2</sub> <sup>j</sup>		2.3				53	36			
(1b) (0.23)	12		0.25		C	10	2.0				65	26			
(1b) (0.2)	13	0.6		NaOMe (0.01)	Pt	-60	2.5				49	25			
(1b) (0.15)	14		0.0	(0.03)							57	43			
(1b)	15			(0.06)							49	38			
(1b) (0.05)	16			(0.01)							45	45			
(1b) (0.15)	17			(0.03)							60	27			
(1b) (0.15)	18	0.0	0.4	CF <sub>3</sub> CO <sub>2</sub> Li (0.3M)							68	18			
(1c) (0.04)	19	0.3				10	1.6				65	18	6	47	2.0 3.0
(1c)	20						2.0				74	28	14	23	0.6 2.0
(1d)	21	0.6					1.4				74	63	11	16	0.2 5.7
(1d)	22					-60	1.4				93	63	3	10	0.2 21.0
(1d)	23	0.3				10	2.0				76	61	13	23	0.3 4.7
(1d)	24						1.6				66	27	5	70	2.2 5.4
(1d)	25			MeCN (12)			2.0				91	51	5	31	0.5 11.0
(1d)	26			(16)							82	34	0	34	0.6
(1d) (0.016)	27										70	67	14	13	0.2 6.0
(1d) (0.12)	28										74	49	7	27	0.4 7.0
(1d) (0.04)	29			Slow stirring (<1 revolution s <sup>-1</sup> )							67	70	6	16	0.2 12.0
(1d)	30	0.0		CF <sub>3</sub> CO <sub>2</sub> Li (0.3M)							88	40	14	39	0.7 2.9
(1d)	31	0.3			C						74	78	0	7	0.1
(1d)	32						1.6				85	61	10	21	0.5 6.1
(1d)	33				PbO <sub>2</sub> <sup>j</sup>		2.0				76	56	9	25	0.4 6.2
(1c)	34				C						69	95	0	0	0
(1f)	35			MeCN (16)			1.0	1.26			60	36	43	0	0 0.8
(1f)	36						0.4	1.26			44	8	73	0	0 0.1
(1f)	37					20	0.46	1.9			19	8	69	0	0 0.1
(1f)	38					-50	0.46	18			4	70	0	0 0.1	
(1f)	39					10	2.0	1.26			47	13	85	0	0 0.2
(1g)	40				Pt		1.2	2.9			61	62	36	2	0.02 1.7
(1g)	41						1.6				81	35	60	0	0 0.6
(1g)	42			MeCN (16)							74	59	76	6	0.1 3.7
(1h) (0.08)	43	0.6	0.2			-60	2.5	2.2			67	65	0	0	0

<sup>a</sup> Sodium hydrogen carbonate is added as buffer to prevent acid-catalysed cleavage of the quinone acetals. The hydrogen carbonate is not all in solution. The concentration indicated is that which would be obtained if all of it went into solution. <sup>b</sup> The potentials were measured relative to a silver wire in experiments 1—18 and 43, relative to a saturated calomel electrode (s.c.e.) containing LiCl (s.c.e.—LiCl) in experiments 19, 20, 23—35, and 40—42, and relative to an Ag—AgS electrode in experiments 21, 22, 36—38, and 43. The correlation between the potentials measured with these reference electrodes and the usual s.c.e. was determined from peak voltammograms of phenol (1h) in methanol (see Experimental section). We found that the potential relative to the s.c.e. can be obtained by addition of -0.01 V to the s.c.e.—LiCl potential, 0.07 V to the Ag-wire potential, and 0.60 V to the Ag—Ag<sup>+</sup> potential. <sup>c</sup> *Q* was chosen such that the conversion would be <50% (except in experiments 36—38). <sup>d</sup> Refers to the yield of methoxylated products based on consumed starting phenol. The traditional chemical yield based on the total amount of starting phenol is obtained by multiplication of the yield in this Table by the conversion. No entry for the yield indicates that it was not determined, but was <5%. <sup>e</sup> *p*-Methoxylation refers to the sum of the yields of compounds (2), (3), (8), and (13). The actual yields of the individual compounds are given in Table 2. <sup>f</sup> *o*-Methoxylation refers to the sum of the yields of compound (4) and its dimer. The actual yield of each compound is given in Table 2. <sup>g</sup> Dimerisation refers to the sum of the yields of compound (6) and the corresponding diphenoquinone (12). The actual yield of each compound is given in Table 2. <sup>h</sup> Only *p*-benzoquinone was isolated. <sup>i</sup> Refers to a graphite anode. <sup>j</sup> Refers to a lead dioxide anode made by anodic precipitation of lead dioxide on a graphite rod.

vs. Ag wire) affords a mixture of (8a) (19%) and 4-methoxy-4-phenylcyclohexa-2,5-dienone (14) (23%) with 100% conversion (Scheme 2). Oxidation of 4-methoxyphenol (1h) under the same conditions only gives (8a). This shows that the phenylated product (14) is formed by phenylation of phenol (*via* nucleophilic attack of benzene on the phenoxylium ion from phenol) followed by anodic methoxylation of the resulting 4-phenylphenol. This is further confirmed by the fact that 4-phenylphenol gives a high yield of (14) on anodic oxidation in methanol.

In order to be able to draw reliable conclusions from the results in Tables 1 and 2 we have tried to estimate the maximum possible experimental error (see Experimental section) in our analytical procedure for determination of conversions and yields. Using these estimates we have calculated the largest possible error in the *p* : *o* and Dim :

in the same direction, as has been assumed. To test this we carried out four experiments on 2,6-di-*t*-butylphenol (1d) in which we tried to maintain the same conditions as in experiment 23 in Table 1. Experimentally we found: conversion (%): 78, 77, 78, and 73 (average 77); *p* (%): 58, 59, 57, and 62 (average 59); *o* (%): 12, 12, 11, and 10 (average 11); Dim (%): 18, 19, 18, and 19 (average 19); *p* : *o* : 4.8, 4.7, 5.2, and 6.1 (average 5.2); Dim : (*p* + *o*) : 0.26, 0.27, 0.26, and 0.26 (average 0.26). This gives a maximum deviation from the mean of 4% for the Dim : (*p* + *o*) ratio and of 17% for the *p* : *o* ratio. We do not believe that this lack of accuracy in the determination of yields is exceptional, and our results suggest that great care should be exercised in using the results of preparative experiments for mechanistic conclusions.

Taking the maximum possible errors from Table 3 into

account it is still possible to extract from Tables 1 and 2 a qualitative relationship between the key experimental variables in the electrolysis experiments and the product

TABLE 2

Products and yields obtained on anodic oxidation of phenols (1a—h) <sup>a</sup> in methanol

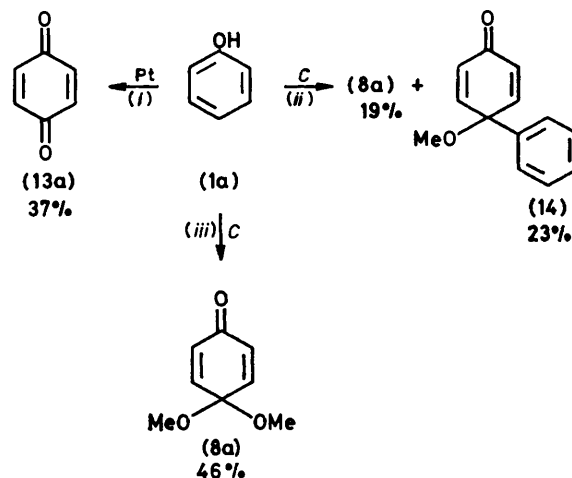
Phenol	Experiment no.	Products (yield, %)
(1a)	1	(13a) (37)
(1a)	2	(8a) (46)
(1c)	19	(8c) (10); (13c) (8); (4c) (6); (6c) + (12c) (47)
(1c)	20	(8c) (18); (13c) (10); (4c) (14); (6c) + (12c) (23)
(1d)	21	(8d) (31); (13d) (3); (3d) (29); (4d) (11); (6d) (14); (12d) (2)
(1d)	22	(8d) (15); (3d) (48); (4d) (3); (6d) (9); (12d) (1)
(1d)	23	(8d) (37); (3d) (24); (4d) (13); (6d) (18); (12d) (5)
(1d)	24	(13d) (16); (3d) (11); (4d) (5); (6d) (30); (12d) (40)
(1d)	25	(8d) (13); (13d) (23); (3d) (18); (4d) (5); (6d) (16); (12d) (15)
(1d)	26	(8d) (32); (3d) (22); (6d) (12); (12d) (22)
(1d)	27	(8d) (32); (3d) (35); (4d) (11); (6d) (13)
(1d)	28	(8d) (20); (13d) (7); (3d) (22); (4d) (7); (6d) (17); (12d) (10)
(1d)	29	(8d) (34); (3d) (36); (4d) (6); (6d) (16)
(1d)	30	(8d) (30); (3d) (10); (4d) (14); (6d) (24); (12d) (15)
(1d)	31	(13d) (38); (3d) (40); (6d) (5); (12d) (2)
(1d)	32	(8d) (36); (13d) (4); (3d) (21); (6d) (8); (12d) (13)
(1d)	33	(8d) (4); (13d) (18); (3d) (34); (4d) (9); (6d) (2); (12d) (23)
(1f)	35	(2f) (36); (4f) (34); the dimer of (4f) (9) <sup>b</sup>
(1f)	39	(2f) (13); (4f) (61); the dimer of (4f) (24) <sup>b</sup>
(1g)	40	(13g) (47); (3g) (15); the dimer of (4g) (36); <sup>b</sup> (12g) (2)
(1g)	41	(13g) (24); (3g) (11); the dimer of (4g) (60) <sup>b</sup>
(1g)	39	(13g) (59); the dimer of (4g) (16); <sup>b</sup> (12g) (6)

<sup>a</sup> Only compound (2b) was isolated in the oxidations of (1b). Oxidation of the phenol (1h) gave only (2h). <sup>b</sup> These dimers are formed by Diels–Alder reaction of compound (4) with itself (see ref. 17).

pattern obtained [expressed in terms of the *p*:*o* and Dim:(*p*+*o*) ratios]. This correlation is shown in Table 4. We emphasise that these conclusions are only valid for oxidations carried out under the same experimental conditions as in this study (see later). To determine whether oxidation of methanol takes place when a phenol is present in the electrolyte, the current was determined as a function of the potential in methanol and in a series of mixtures of methanol and acetonitrile with and without addition of a phenol. The results are displayed in the Figure.

The results in Tables 1 and 2 show that anodic oxidation of phenols in methanol can be a very versatile and simple synthetic method allowing selective preparation of *ortho*- and *para*-methoxylated products, or quinones, or dimers, from the same substrate by appro-

prate variation of the experimental conditions. With this in mind we carried out a series of preparative-scale experiments the results of which are given in Table 5.



SCHEME 2 (i) Experiment 1 in Table 1. (ii) Carried out on a 0.15M-solution of phenol in methanol–benzene (1:1) containing LiClO<sub>4</sub> (0.3M) and NaHCO<sub>3</sub> (0.4M) at a constant potential (*E* 2.0 V relative to Ag wire) and a temperature of 10 °C. (iii) Experiment 2 in Table 1

*Mechanism of Anodic Oxidation of the Phenols (1a—h) on a Platinum Anode in Methanol.*—The anodic discharge potential of methanol is of the same magnitude as

TABLE 3

Maximum error in the analytical yields (*p*, *o*, and Dim) and in the *p*:*o* and Dim:(*p*+*o*) ratios given in Table 1

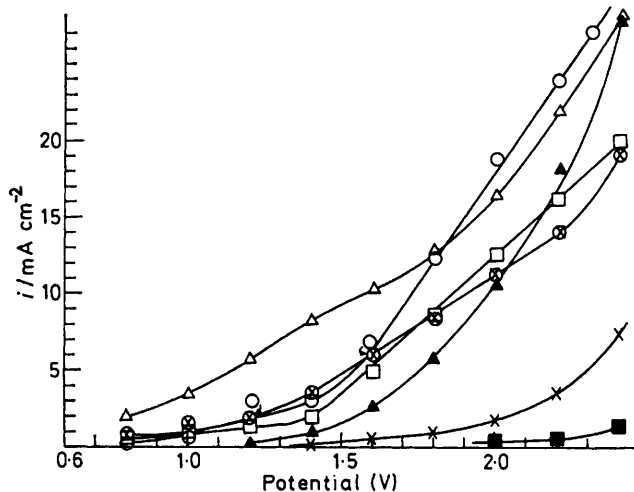
Phenol	Maximum error (%) in					
	Conversion	<i>p</i> -Methoxyl-ation ( <i>p</i> )	<i>o</i> -Methoxyl-ation ( <i>o</i> )	Dimeris-ation (Dim)	Dim:( <i>p</i> + <i>o</i> ) <i>p</i> : <i>o</i>	
(1a)	0	13				
(1b) <sup>a</sup>	15	35				
(1b) <sup>b</sup>	18	23				
(1c)	9	33	33	13	28	24
(1d)	5	16	20	17	12	14
(1e)	4	12				
(1f) <sup>c</sup>	17	35	30			20
(1f) <sup>d</sup>	11	26	23			16
(1g)	5	7	21	17	26	26

<sup>a</sup> For experiments carried out with a Pt anode. <sup>b</sup> For experiments carried out on a graphite anode. <sup>c</sup> For experiments carried out in pure MeOH. <sup>d</sup> For experiments carried out in MeCN–MeOH.

that of the phenols (1a—h). It is therefore possible that the oxidation of the phenols (1a—h) in methanol follows an indirect path involving initial oxidation of methanol to a methoxyl radical or some other species formed by oxidation of methanol.<sup>6</sup> This methoxyl radical could oxidise the phenol by hydrogen abstraction [path (i) in Scheme 3] or by electrophilic attack [path (ii) in Scheme 3]. A third mechanism [path (iii) in Scheme 3] involves coupling of a methoxyl radical with the phenoxy radical

<sup>6</sup> N. L. Weinberg in 'Technique of Electroorganic Synthesis,' Part I, ed. N. L. Weinberg, Wiley–Interscience, New York, 1974, p. 254.

(15) which can be formed either *via* path (i) or by concurrent anodic oxidation of the phenol. The results in Figure 1 and similar results for the other phenols investigated show that the anodic methoxylation of phenols (1a—h) does not occur *via* either of the mechanisms (ii) or (iii).<sup>\*</sup> In both paths the anodically generated methoxyl radicals are consumed without regeneration of methanol and the rate of formation of



Current-potential curves for methanol and methanol-acetonitrile mixtures with and without phenol (1d) added. The measurements were carried out under the same conditions as in experiment 23 (platinum anode) and experiment 31 (graphite anode) in Table 1. All potentials were measured *versus* a s.c.e. (LiCl). LiClO<sub>4</sub> (0.3M) was the supporting electrolyte and NaHCO<sub>3</sub> (0.4 M) was added in all experiments. The concentration of phenol (1d) was always 0.04M. All points on each curve were measured within 5 min from the start of the experiment beginning with the determination at 2.4 V (30 s were allowed to pass after each potential setting in order to get a stable current value). Therefore only a small fraction of the phenol was oxidised during a series of measurements and the phenol concentration is approximately the same in all measurements. (×) Methanol, Pt anode. (⊗) Methanol with (1d) added, Pt anode. (■) Methanol:acetonitrile = 1:2, Pt anode. (□) Methanol:acetonitrile = 1:2 with (1d) added, Pt anode. (○) Methanol:acetonitrile = 1:11 with (1d) added, Pt anode (the background current for this mixture is slightly lower than for the 1:2 mixture). (▲) Methanol, graphite anode. (△) Methanol with (1d) added, graphite anode.

methoxylated products cannot exceed the rate of formation of methoxyl radicals, which in its turn is determined by the potential and the methanol (methoxide ion) concentration. If therefore steps (b) or (c) were dominant, the addition of phenol (1d) should at most increase the current † at a given potential by a factor of 2–4. However, from Figure 1 it can be seen that addition of phenol (1d) to methanol or methanol-acetonitrile results in a very large current increase which can only be explained by a direct oxidation of the phenol or a catalytic oxidation [path (i) in Scheme 3]. The data in the Figure also exclude path (i) as a product-forming route of any importance since the total current has little dependence

<sup>\*</sup> The following argument is based on results obtained for phenol (1d). However since similar results were obtained for the other phenols the conclusions are also valid for them.

on the methanol concentration when a phenol is present in the electrolyte. Furthermore, though methanol is

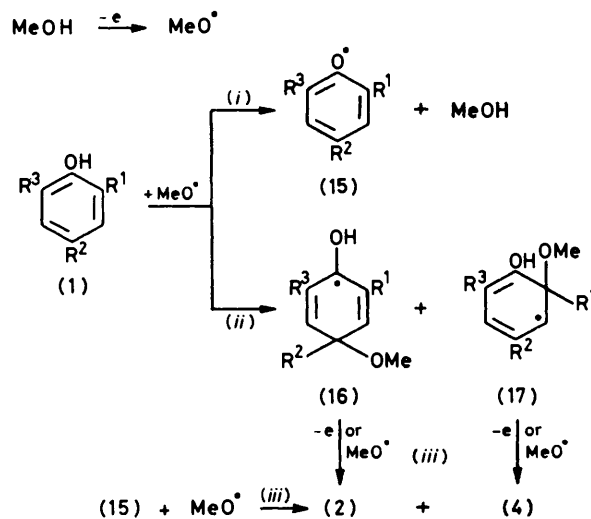
TABLE 4

Correlation between changes in the key experimental variables and the ratios Dim : (*p* + *o*) and *p* : *o* in the anodic oxidation of phenols (1a—h)<sup>a</sup>

Variable	Change from	to	Dim : ( <i>p</i> + <i>o</i> )	<i>p</i> : <i>o</i>
Potential	1.6 V <sup>b</sup>	2.0 V <sup>b</sup>	—	?
Anode	Pt	Graphite	—(—)	<i>c</i>
Anode	Pt	PbO <sub>2</sub>	≈	≈
Solvent	MeOH	MeOH-MeCN	≈ or +	++
Phenol concentration (M)	0.016	0.12	+	?
Stirring rate (rev. s <sup>-1</sup> )	4	<1	—	++
Temp. (°C)	10	-60	<i>d</i>	?
Supporting electrolyte	LiClO <sub>4</sub>	Li(O <sub>2</sub> CCF <sub>3</sub> )	+	—
Substituents	<i>p</i> -Me	<i>p</i> -MeO	—	+
	<i>o</i> -Me	<i>o</i> -MeO	—	—
	<i>p</i> -Me	<i>p</i> -Ph	—	?

<sup>a</sup> ++ Indicates a large increase and + a smaller though reproducible increase. — And — have the same significance for decreases. ≈ Indicates no change. ? Indicates that no consistent change is observed in going from phenol (1a) to (1g). <sup>b</sup> Measured relative to the s.c.e. (LiCl) electrode. <sup>c</sup> A cathode with a larger surface area was used when graphite was the anode. Therefore, from the data in Table 1 we cannot draw any conclusions about the influence of the anode material on the *p* : *o* ratio. <sup>d</sup> The yield of (2b) from the oxidation of (1b) on a graphite anode is not affected by the temperature. However, when a platinum anode is used the yield of (2b) increases when the temperature is lowered.

regenerated in path (i), methanol or methoxyl radicals must be consumed in the actual methoxylation step so



SCHEME 3

that there will be a decrease in the methanol concentration in the double layer. We therefore conclude that

† If we assume a mixed oxidation process, that is if (2), (4), (15), (16), or (17) is oxidised further electrochemically, then there can be as much as a four-fold increase of the current on addition of the phenol. However, this still only accounts for *ca.* 6% of the current increase observed on addition of (1d) to methanol-acetonitrile (1:11) at a potential of 2.0 V.

the major product-forming steps in the anodic oxidation of phenols in methanol involve an initial direct electron transfer from the phenol to the anode. It is well known from other investigations that many aromatic<sup>6,7</sup> and

exclude the involvement of methoxyl radicals in the formation of the product. However, the product distribution obtained with graphite anodes is almost the same as obtained with platinum anodes, the total current has

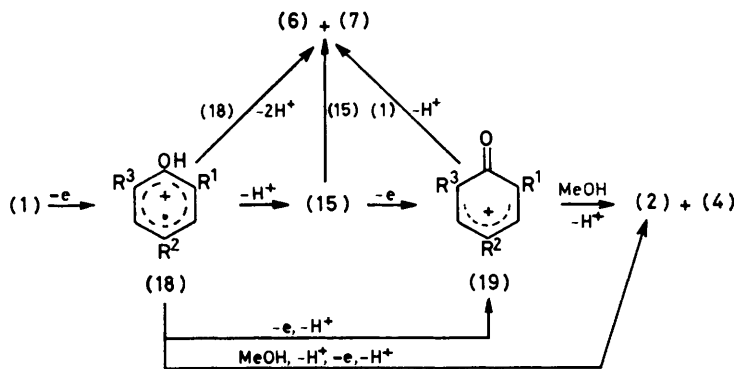
TABLE 5  
Preparative oxidation of the phenols (1c), (1d), (1h), and *p*-phenylphenol<sup>a</sup>

Phenol, g; mol: (M)	MeOH (ml)	LiClO <sub>4</sub> [g: (M)]	Base, [g: (M)]	Anode (cm <sup>2</sup> )	Cathode (cm <sup>2</sup> )	Potential (V)	Q/F mol <sup>-1</sup>	Conversion (%)	Products, <sup>b</sup> yield (g: %)
(1c) [6; 0.49; 0.44]	100 <sup>c</sup>	4; 0.34	<i>sym</i> -Collidine (0.8; 0.005)	C(90)	W (1.6) Steel <sup>a</sup>	1.27 <sup>d</sup>	6.1 <sup>e</sup>	100	(13c) (3.34; 50)
(1d) [5; 0.024; 0.048]	500	5; 0.09	NaHCO <sub>3</sub> (5; 0.12)	Pt(50)	Ni (5.7)	2.2 <sup>e</sup>	3.4	95	(8d) (3.0; 47) (4d) (0.05; 1)
(1d) [10; 0.048; 0.44]	110	4; 0.34	<i>sym</i> -Collidine (1; 0.006)	C(90)	W(1.6)	2.0 <sup>e</sup>	5.6	100	(8d) (10; 77)
(1h) <sup>f</sup> [10; 0.08; 1.34]	60	4; 0.63		Pt(50)	W(0.6)	<i>g</i>	3.6	96	(8h) (11.5; 93)
<i>p</i> -Phenylphenol [3; 0.018; 0.29]	60	1; 0.16		Pt(50)	W(0.6)	<i>h</i>	4.0	100	(14) (3.06; 87)

<sup>a</sup> For details see Experimental section. <sup>b</sup> The products were actually isolated and purified. The yields are based on starting material (chemical yields). <sup>c</sup> Benzene (12 ml) was added to the electrolyte. <sup>d</sup> Ag/Ag<sup>+</sup> reference electrode. <sup>e</sup> s.c.e. (LiCl) reference electrode. <sup>f</sup> Taken from ref. 5. <sup>g</sup> Constant current electrolysis (10 mA cm<sup>-2</sup>). <sup>h</sup> Constant current electrolysis (6 mA cm<sup>-2</sup>).

unsaturated<sup>8</sup> compounds are oxidised in preference to methanol although their discharge potential is more anodic than that of methanol. This is generally explained by assuming a preferential adsorption of the unsaturated compound on the anode surface so that there is a very low concentration of methanol in the double layer.

little dependence on the methanol concentration when a phenol is present, and the current yield is even better for graphite than for platinum anodes (methoxyl radicals should undergo further oxidation or dimerise, which should diminish the current yield). We therefore conclude that oxidation of the phenols (1a—h) on a graphite



SCHEME 4

As pointed out above, the appearance of the voltammograms of methanol and the phenols (1a—h) indicates that the charge transfer from methanol to the anode is much slower than for the phenols. This should further enhance the preferential oxidation of the phenols. It might even be that oxidation of methanol does not take place at all in the presence of a phenol, since the intermediates in the oxidation of a phenol are very reactive towards methanol. Hence, all methanol molecules would be consumed in a chemical reaction before they reach the anode surface.

**Mechanism of Anodic Oxidation of the Phenols (1a—h) on a Graphite Anode in Methanol.**—The data in the Figure show that the background current is much larger for graphite than for platinum anodes. Although addition of a phenol to the electrolyte produces a substantial increase in current (Figure), especially at potentials <2.3 V and even when graphite is the anode, we cannot

anode in methanol occurs *via* direct charge transfer. Our finding that phenol can be phenylated in methanol—benzene indicates that the preferential oxidation of the phenols on a graphite anode can be due to selective adsorption of aromatic substrates.

**Formation of Methoxylated Products.**—Four different pathways (see Scheme 4) can be envisaged for the anodic formation of methoxylated products. Nucleophilic attack of methanol on an anodically generated cation radical (18) followed by deprotonation and further oxidation gives (2) and/or (4). Depending on the substituents, (2) and (4) can aromatise and then undergo further anodic oxidation (see Scheme 1). It is, however, unlikely that nucleophilic attack of methanol on (18) can compete with deprotonation (with methanol as base) to

<sup>7</sup> A. Nilsson, U. Palmquist, T. Pettersson, and A. Ronlän, following paper.

<sup>8</sup> T. Shono and A. Ikeda, *J. Amer. Chem. Soc.*, 1972, **94**, 7892.

the phenoxyl radical (15). The cation radical (18) is a strong acid, and deprotonation in a hydroxylic solvent is diffusion-controlled.<sup>9</sup> Furthermore, chemical oxidation of the phenols (1a—h) with one-electron oxidants like iron(III) chloride and cerium(IV) sulphate in methanol gives much higher yields of dimeric products than the electrochemical reaction;<sup>10</sup> this shows that methoxylation of the cation radical is not an important reaction. For the same reason we can also exclude formation of methoxylated products *via* nucleophilic attack of methanol on the phenoxyl radical (15). This leaves us with two pathways, both of which terminate by nucleophilic attack of methanol on the phenoxylum ion (19). The difference between the two paths lies in the mode of generation of the phenoxylum ion. In the first case it is formed by anodic oxidation of the cation radical (18) followed by deprotonation. This path can only be of importance at very high potentials as phenol cation radicals are oxidised at a potential at least 0.9 V more anodic than that for the corresponding phenol.<sup>9,11</sup> In the second case the phenoxylum ion is formed by deprotonation of the cation radical (18) followed by anodic oxidation. This we believe to be the most important path for formation of methoxylated products.

*Formation of Dimeric Products.*—In Scheme 4 we suggest three different mechanisms for the formation of dimeric products [(6) and (7)]: dimerisation of the cation radical (18), dimerisation of the phenoxyl radical (15), and electrophilic attack of the phenoxylum ion (19) on the starting phenol. From the discussion earlier it appears that the first reaction is improbable. Further, we have demonstrated<sup>9</sup> that reversible oxidation potentials for phenols can be measured in strongly acidic media at low temperature and these reversible potentials are about 0.3 V more anodic than the corresponding irreversible potentials measured in methylene chloride. This cathodic shift we ascribe to a rapid deprotonation of the cation radical. From the magnitude of the shift we could determine the first-order rate constant for the deprotonation reaction (diffusion controlled). If, for the sake of argument, we assume that the subsequent chemical reaction is dimerisation of the cation radical, we would expect a smaller cathodic shift of the irreversible peak potential for 2,6-substituted phenols. It is reasonable to assume that the rate of dimerisation of the phenol cation radicals should follow the same trend as that for phenoxyl radicals. However, almost the same cathodic shift is found for all the phenols studied. Since the irreversible peak potentials of the phenols (1a—h) which can be measured in methanol are the same as those measured in acetonitrile, we believe that deprotonation is the only important reaction of the cation radical in methanol.

\* Assumed to be irreversible.

† The dimers could also to some extent be formed by coupling between the phenoxyl radical (15) and the cation radical (18) (Scheme 4) provided that this reaction is very fast.

<sup>9</sup> O. Hammerich, V. D. Parker, and A. Ronlán, *Acta Chem. Scand.*, 1976, **B30**, 89.

In our study<sup>2</sup> of the anodic hydroxylation of phenols we argued that the dimers encountered were formed *via* the third mechanism. The Dim : (*p* + *o*) ratio decreases with increasing potential. At first sight this seems to support the phenoxylum-ion mechanism since an increase in the potential decreases the phenol concentration in the double layer while the methanol concentration is unchanged. However, closer examination of the dimerisation reaction of (15) shows that the Dim : (*p* + *o*) ratio should decrease with increasing potential even if the dimers are formed by this reaction. The ratio between the rate of dimerisation\* and the rate of further oxidation is  $k_{\text{Dim}}c_{\text{R}}/k_{\text{e}}$  where  $k_{\text{Dim}}$  is the rate constant for the dimerisation reaction of (15),  $c_{\text{R}}$  the concentration of (15) in the double layer, and  $k_{\text{e}}$  the rate constant for the charge-transfer reaction from (15) to the anode.  $k_{\text{e}}$  increases exponentially with increasing potential,  $k_{\text{Dim}}$  is independent on the potential, and  $c_{\text{R}}$  is expected to decrease with increasing potential since the phenoxyl radical (15) is more easily oxidised than the starting phenol (1). The Dim : (*p* + *o*) ratio must therefore decrease with increasing potential. It should be possible to distinguish the radical-coupling mechanism from the phenoxylum-ion mechanism by investigation of the dependence of the Dim : (*p* + *o*) ratio on the methanol concentration. In the former reaction the Dim : (*p* + *o*) ratio is determined by the value of  $k_{\text{Dim}}c_{\text{R}}/k_{\text{e}}$ , and changes in the methanol concentration should have little or no effect. In the latter case both coupled and methoxylated products are formed by reaction of the phenoxylum ion (19) and we should observe a marked dependence of the Dim : (*p* + *o*) ratio on the methanol concentration. Examination of the data in Table 1 shows little dependence of the Dim : (*p* + *o*) ratio on the methanol concentration, indicating that the dimers are formed *via* the usual phenoxyl radical coupling reaction.† This conclusion is further supported by literature data<sup>12</sup> on rate constants,  $k$ , for the radical-coupling reaction of the various phenoxyl radicals. For the phenoxyl radicals derived from the phenols (1a), (1b), (1c), (1d), (1h), and 4-phenylphenol,  $\log k$  is (measured in benzene): 8.7, 9.2, 8.6, 7.5, 7.2, and 7.5. The phenols giving the lowest Dim : (*p* + *o*) ratio are those with the lowest rate constant for dimerisation. In agreement with this the phenol (1g) does not give any *meta*–*para* coupled products as would be expected from nucleophilic attack of (1g) on the phenoxylum ion (19g).

*Effects of Changes in Potential, Anode Material, Methanol Concentration, Phenol Concentrations, Supporting Electrolyte, Temperature, Added Base, and Phenol Substituents on the Product Distribution.*—The effects of changes in potential and methanol or phenol concentration on the Dim : (*p* + *o*) ratio are those expected from the mechanism outlined above. However, a doubling

<sup>10</sup> A. Ronlán, *Chem. Comm.*, 1971, 1643.

<sup>11</sup> A. Ronlán, J. Coleman, O. Hammerich, and V. D. Parker, *J. Amer. Chem. Soc.*, 1974, **96**, 845.

<sup>12</sup> S. A. Weiner, *J. Amer. Chem. Soc.*, 1972, **94**, 581; L. R. Mahoney and S. A. Weiner, *ibid.*, p. 585.

of the phenol concentration at a given potential results in a current increase of only about 40% whereas a doubling might be expected. This we ascribe to a decrease of the real potential between the anode and the electrolyte caused by an increased potential drop between the anode and the reference electrode (the potentiostat does not correct for changes in the resistance of the electrolyte). This increase in the potential drop is mainly caused by the increase in the current flowing through the cell. In preparative experiments fairly large currents are drawn and the error in the potential measurement in our experiments with a current of 1 A is *ca.* 0.2 V. Adsorption of the phenol on the anode surface might also affect the potential drop. In general it is difficult to decide whether an effect caused by a change in the composition of the electrolyte is 'real' or caused by a potential change, following a change of the potential drop between the reference and the anode.

We cannot give any straightforward explanations for the dependence of the *p* : *o* ratio on the potential, the methanol concentration, or the stirring rate [the substituent effect can be explained in terms of the stabilising effect of the substituent on the intermediate phenoxylium ion (19)]. It is possible that *ortho*-methoxylation occurs *via* an intramolecular nucleophilic attack on the phenoxylium ion of a methanol molecule which is hydrogen-bonded to the oxygen of the phenoxylium ion (and was hydrogen-bonded to the phenol precursor). In methanol-acetonitrile the phenol and the corresponding phenoxylium ion are solvated by both methanol and acetonitrile and the intramolecular reaction (which is much faster than the corresponding intermolecular one) becomes less favoured. The stirring rate dependence of the *p* : *o* ratio might be explained in a similar way. An increase of the stirring rate increases the methanol concentration and therefore the methanol-phenol aggregate concentration in the double layer.

Our finding that the Dim : (*p* + *o*) ratio is smaller for graphite than for platinum anodes shows that the rate of oxidation of phenoxy-radicals to the corresponding phenoxylium ions must be greater on graphite than on platinum anodes. This in turn could be caused by a higher energy of adsorption of phenoxy radicals on graphite than on platinum. A similar difference was observed in our study of the anodic hydroxylation of phenols.<sup>2</sup>

Only a few experiments were carried out in which the temperature dependence of the *p* : *o* and the Dim : (*p* + *o*) ratios was investigated. Both the *ortho*- and the *para*-methoxylated products are formed by nucleophilic attack of methanol on the phenoxylium ion (19). Therefore the temperature dependence of the *p* : *o* ratio must

\* A quantitative treatment requires knowledge of the overpotential ( $\eta$ ) for the anodic oxidation of the phenoxy radical to the phenoxylium ion and the activation energy [ $E^*(\text{ox})$ ] for the corresponding chemical oxidation of the phenoxy radical since the rate constant for the anodic oxidation can be expressed as  $^{13} K \cdot \exp\{(1 - \beta)F\eta - E^*(\text{ox})/RT\}$ . From this it can be seen that if the activation energy [ $E^*(\text{c})$ ] for a competing chemical reaction is of the same magnitude as, or greater than,  $E^*(\text{ox})$  the electrochemical reaction should be favoured by a temperature decrease.

be derived from the difference between the activation energy [ $E^*(p)$ ] of the *para*-methoxylation reaction and the activation energy [ $E^*(o)$ ] of the *ortho*-methoxylation reaction [equation (A)]. Here  $K_p$  and  $K_o$  are pre-exponential factors and  $k_p$  and  $k_o$  are the rate constants

$$\ln(p/o) \approx \ln(k_p/k_o) = \ln(K_p/K_o) + [E^*(o) - E^*(p)]/RT \quad (A)$$

for the *para*- and the *ortho*-methoxylation reactions. From this equation it can be seen that if  $E^*(o) > E^*(p)$  then the *p* : *o* ratio increases with decreasing temperature and *vice versa*. This is illustrated by electrolyses of the phenol (1f), at 20 and  $-50^\circ\text{C}$  (experiments 37 and 38, Table 1). At  $20^\circ\text{C}$  the *p* : *o* ratio was 0.12 : 1. Using this value the *p* : *o* ratio can be calculated at all other temperatures from the equation above. At  $-50^\circ\text{C}$  the calculated value of the *p* : *o* ratio is 0.06 : 1, which is the same as the value determined experimentally. From analytical (Table 1) and preparative (Table 5) experiments the following qualitative relationship between  $E^*(o)$  and  $E^*(p)$  and the phenol substituents was derived:  $E^*(p)$  (*para*-OMe) <  $E^*(o)$  (*ortho*-OMe) <  $E^*(p)$  (*para*-Me) <  $E^*(o)$  (*ortho*-Me)  $\approx$   $E^*(p)$  (*para*-H)  $\ll$   $E^*(o)$  (*ortho*-H), where  $E^*(p)$  (*para*-OMe) is the activation energy for the nucleophilic attack of methanol on the *para*-position of a phenoxylium ion (19) substituted with a *p*-methoxy-group, *etc.* In accordance, we found that the *p* : *o* ratio increased for the phenol (1b) and decreased for the phenol (1f) when the electrolysis temperature was lowered. For (1d) we observed a large increase of the *p* : *o* ratio when the temperature was lowered, showing that  $E^*(p)$  (*para*-H) <  $E^*(o)$  *ortho*-Bu<sup>t</sup>. In general the Dim : (*p* + *o*) ratio decreases with decreasing temperature, which is to be expected since chemical reactions are often more affected by temperature changes than are pure charge-transfer reactions.\*

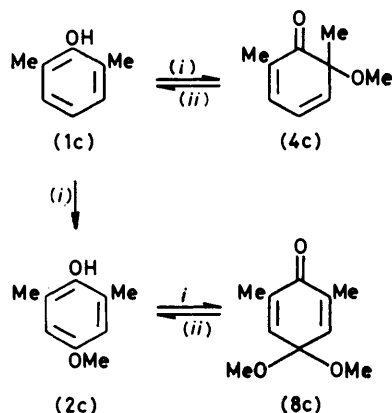
*Effect of Cathode Area on the p : o ratio and the Current Yield.*—The data in Table 5 and to some extent those in Table 1 show that the size of the cathode has a significant influence on the current yield; for 2,6-substituted phenols it also affects the product distribution (*p* : *o* ratio). A large cathode gives lower current yields and higher *p* : *o* ratios than a small cathode. This can be explained by a simultaneous cathodic reduction of the anodically formed dienones. From previous investigations<sup>2,5</sup> we know that dienones are very easily reduced at the cathode. The reactions in Scheme 5 explain why the *p* : *o* ratio is affected by the cathode size in the case of a 2,6-substituted phenol [exemplified by (1c)]. The *para*-methoxyphenol (2c) formed in the first step of the *para*-methoxylation reaction cannot be reduced cathodically back to (1c). Only the dienone (8c) formed by anodic oxidation of (2c) is reduced at the cathode to (2c). Thus for the *para*-methoxylation reaction it is only the current yield and not the total yield of (2c) and (8c) (*p*) † that is

† The relative amounts of (2c) and (8c) are strongly affected. A large cathode gives mainly (2c) whereas a small cathode gives mainly (8c).

<sup>13</sup> J. O'M. Bockris and D. M. Drăzić, 'Electrochemical Science,' Taylor and Francis, London, 1972, p. 86.



affected by the cathode size. In contrast, the *ortho*-dienone (4c) formed in the first step of the *ortho*-methoxylation reaction is reduced at the cathode back to the starting phenol (1c). With a sufficiently large cathode an



SCHEME 5 (i) Anodic methoxylation, that is loss of two electrons and two protons and addition of one molecule of methanol. (ii) The reverse process occurring at the cathode

equilibrium is established with a fairly low concentration of (4c). However, (1c) is being consumed continuously in the *para*-methoxylation reaction, resulting in predominant formation of *para*-methoxylated products [mainly (2c)]. If the cathodic reduction of (4c) and (8c) is suppressed by using a small cathode and if the electrolysis is carried out at high potential and low conversion, 'kinetic' control is established and the *p* : *o* ratio reflects the ratio between the rates of formation of (2c) and (4c).\*

For the *para*-alkylphenols with one or two unsubstituted *ortho*-positions [(1b), (1f), and (1h)] the effect of cathode size on the *p* : *o* ratio is not always reversed as one might expect, since in these cases the initial *ortho*-methoxylated product (5) cannot be reduced to (1). With phenol (1h) as substrate only *para*-methoxylated products (2h) were isolated; with phenol (1b) small amounts of *ortho*-methoxylated products could be detected (see Table 1), and with (1f) appreciable amounts of *ortho*-methoxylated products were formed. This shows that the *ortho*-methoxylation reaction [nucleophilic attack of methanol on the phenoxylium ion (19)] is slow (has higher activation energy) compared with the *para*-methoxylation reaction unless one or both *ortho*-positions are substituted with an alkyl or alkoxy-group. From our results the relationship between activation energies and phenol substituents described above can be deduced. For the phenols (1b) and (1h) the difference

\* In one experiment (1c) was oxidised on a carbon anode in a cell with a small cathode (0.6 cm<sup>2</sup>). A 2 : 1 mixture of (8c) and (4c) was obtained in 90% yield ( $Q = 2.5 \text{ F mol}^{-1}$ ; conversion 100%). At the end of the electrolysis the cathode was substituted for a larger one (2.4 cm<sup>2</sup>) and the electrolysis was continued as before. At regular intervals the electrolyte was examined by ultraviolet spectroscopy. We found that the dienones (4c) and (8c) gradually disappeared whereas the concentration of (2c) increased continuously. When all the (4c) and most of the (8c) had disappeared the small cathode was fitted into the cell again. Further electrolysis converted (2c) into (8c). No (4c) was detected.

between the activation energies of the *ortho*- and *para*-methoxylation reactions completely masks any effect of cathode size on the *p* : *o* ratio. However, for the phenol (1f) the activation energies are of the same magnitude and in accord we find that the *p* : *o* ratio is affected by the cathode size (decreases with increasing cathode size).

Discussion of the reduction of the dienones (2b), (2e), (2f), (2h), and (4c—g) back to the starting phenols (1a—g) at the cathode was deferred in dealing above with the effect of changes in the experimental variables.

The total cathodic current (equal to the cell current  $i$ ) is the sum of the background reduction current ( $i_a$ ) and the dienone reduction current ( $i_d$ ). In most of our reductions  $i_d = \text{a constant} = i_{d,\text{lim}}$  (where  $i_{d,\text{lim}}$  is the diffusion-controlled limiting current for the dienone reductions).<sup>†</sup> Therefore the ratio  $i_{d,\text{lim}} : i$  determines the extent to which the dienone reductions can affect the Dim : (*p* + *o*) and *p* : *o* ratios. When  $i \gg i_{d,\text{lim}}$  the dienone reductions are of little importance. Unfortunately we do not know  $i_{d,\text{lim}}$  and we cannot determine from the total current (potential) whether the dienone reductions have affected the Dim : (*p* + *o*) or *p* : *o* ratio. However the maximum effect of the cathodic reduction of the dienones on the Dim : (*p* + *o*) and *p* : *o* ratios in changing the experimental variables can be estimated. For example in the oxidations of phenols (1c) and (1d), we can assume that the decrease in the yields of the *ortho*-dienones (4c) and (4d) in going from 2 to 1.6 V anode potential (experiments 19, 20 and 23, 24) results in a corresponding increase in the dimer yield (*i.e.* all the *ortho*-dienone which is reduced back to the starting phenol is converted into the dimer by further oxidation). This still accounts only for a smaller part of the change in the Dim : (*p* + *o*) ratio. Furthermore the Dim : *p* ratio, which should be independent of the cathodic reduction of (4c) and (4d) (the reduction of the *para*-dienones does not give the starting phenol), changes drastically with changes in the anode potential. This shows that the change observed in the Dim : (*p* + *o*) ratio when the anode potential changes is indeed caused by the potential change. The rate of reaction of the phenoxylium ion (19) with methanol and therefore the *p* : *o* ratio should not be greatly dependent on the anode potential. The fairly large changes in the *p* : *o* ratio with anode potential are probably caused by changes in the  $i_d : i$  ratio. This is supported by the data in Table 1 which show that an increase in the anode potential (increase in  $i$ ) generally leads to an increase in the current yield. If, for phenol (1g), we assume that the *p* : *o* ratio (0.6 : 1) found at 1.6 V anode potential (experiment 41) is the true ratio ( $i \gg i_{d,\text{lim}}$ ), reflecting the difference in rate between the *ortho*- and *para*-methoxylation reactions, we can calculate the additional current (decrease in current yield) required to obtain the *p* : *o* ratio of 1.7 : 1 at 1.2 V anode

<sup>†</sup> When a small cathode is used  $i_{d,\text{lim}}$  is probably comparatively small. In case  $i_d < i_{d,\text{lim}}$  the effect of the cathode potential on the rate constant for the dienone reduction should also be taken into account.

potential (experiment 40), if the change is caused solely by the reduction of (4g) to (1g). This is equivalent to assuming that the rates of *ortho*- and *para*-methoxylation are independent of potential. We find, provided only (4g) is reduced and not (8g), that 2.6 F mol<sup>-1</sup> of current should be consumed. In experiment 40, 2.5 F mol<sup>-1</sup> of current was consumed showing that the observed change in the *p* : *o* ratio with anode potential can be explained solely by the cathodic reduction of (4g) to (1g). For phenols (1c) and (1d) the *p* : *o* ratio shows little potential dependence (experiments 19, 20, and 23, 24) but the current yield is reduced when the anode potential is decreased ( $i_{a,lim}/i$  increases). With these particular phenols the corresponding *ortho*-dienones [(4c) and (4d)] are presumably more difficult to reduce than the *para*-dienones [(8c) and (8d)] because of steric hindrance. The dienones (8c) and (8d) are reduced to (3c) and (3d). This reduction affects only the current yield, not the *p* : *o* ratio.

By similar arguments we can show that the effects of adding acetonitrile to the electrolyte (experiments 25 and 26, 35 and 36, and 41 and 42) are caused mainly by changes in the relative rates of the dimerisation and *ortho*- and *para*-methoxylation reactions.

**Synthetic Applications.**—The results of the preparative scale experiments (Table 5) indicate that the analytical yields in Table 1 can also be obtained or even improved in scaled-up electrolyses. *para*-Methoxylation is feasible and of preparative interest for all phenols. Phenol itself can be converted into the dimethoxy hemiacetal of *p*-benzoquinone (8a) in 46% yield. 4-Alkyl- or 4-alkoxyphenols give 4-alkyl-4-methoxy- or 4,4-dimethoxycyclohexa-2,5-dienones (8) in 45–97% yield. 4-Unsubstituted phenols give 4,4-dimethoxycyclohexa-2,5-dienones in 50–90% yield. These dienones can be converted into the corresponding quinone by acid-catalysed hydrolysis or to the corresponding *p*-methoxyphenol by cathodic reduction. *ortho*-Alkyl or *ortho*-alkoxyphenols also give *ortho*-methoxylation. However, it appears that useful yields of *ortho*-methoxylated products can only be obtained if one or both *ortho*-positions of the starting phenol are substituted with an alkoxy-group (with these phenols it is probably not possible to achieve exclusive *para*-methoxylation). The *ortho*-dienones undergo a fairly rapid Diels–Alder reaction with themselves and can usually not be isolated. However, if another electroinactive diene or dienophile is added to the electrolyte a preparatively useful, mixed Diels–Alder reaction could be achieved. As the dimerisation of the *ortho*-dienones appears to occur mainly during work-up it should be possible to bring about reaction of the electrolytic product with an easily oxidised diene or dienophile added immediately after the electrolysis.

#### EXPERIMENTAL

The n.m.r. analyses were carried out with a JEOL PMX60 instrument using SiMe<sub>4</sub> as internal reference. The mass spectra were determined using an LKB-6000 spectrometer. The potentiostat was built in our laboratory. The solvents

used were reagent grade stored over molecular sieves (Linde 3A); the phenols (1a–h) were commercial products. The electrolysis cell used in the analytical and in some of the preparative experiments was a cylindrical vessel (height 70 mm, diameter 41 mm) fitted with a Teflon-coated stirring bar (length 33 mm, diameter 7 mm) and a Teflon lid with holes allowing the three electrodes to be placed in exactly the same relative position in all experiments. Six different electrode combinations were used (the areas given for the electrodes are the effective areas) as follows. (a) A cylindrical platinum foil anode (50 cm<sup>2</sup>) and a tungsten wire cathode (length 40 mm, diameter 2 mm, area 2.5 cm<sup>2</sup>) positioned on the centre line of the anode together with a standard calomel electrode (s.c.e.) (LiCl) reference (Radiometer K901). The s.c.e.(KCl) used was the Radiometer K401 positioned with the tip 2 mm from the inside of the anode. This arrangement was used in the oxidation of the phenols (1c), (1d), (1f), and (1g).

(b) As in (a) but with a silver wire (length 40 mm, diameter 2 mm) reference electrode positioned vertically at a distance of 2 mm from the inside of the anode. This arrangement was used in the oxidations of phenols (1a), (1b), and (1h).

(c) A cylindrical graphite (Union Carbide AUC-graphite) rod (length 40 mm, diameter 16 mm, area 20 cm<sup>2</sup>), a tungsten wire cathode (length 400 mm, diameter 0.5 mm, area 6.3 cm<sup>2</sup>) coiled around the anode at a distance of 12 mm, and a s.c.e.(LiCl) reference positioned with the tip 2 mm from the anode. This rearrangement was used in the oxidations of phenols (1d) and (1f).

(d) A cylindrical graphite (AUC) rod anode (length 40 mm, diameter 25 mm, area 31 cm<sup>2</sup>), a tungsten wire cathode (6.3 cm<sup>2</sup>) coiled around the anode at a distance of 8 mm, and the silver wire reference electrode positioned 2 mm from the anode. This arrangement was used for the oxidation of phenols (1a), (1b), (1e), and (1h).

(e) A hollow graphite (AUC) cylinder anode (internal diameter 31 mm, length 100 mm, area 90 cm<sup>2</sup>), a tungsten wire cathode (diameter 0.3 mm, length 100 mm, area 1.6 cm<sup>2</sup>) placed on the centre line of the anode, and a Ag–Ag<sup>+</sup> reference electrode positioned with the tip 2 mm from the inside of the anode. This arrangement was used in experiments 36–38.

(f) A cylindrical lead dioxide rod (length 40 mm, diameter 17 mm, area 21 cm<sup>2</sup>) prepared by electrochemical precipitation of lead dioxide on a graphite rod,<sup>2</sup> a tungsten wire cathode (6.3 cm<sup>2</sup>) positioned as in (c), and the s.c.e.(LiCl) reference positioned 2 mm from the anode.

The equipment used for measuring peak voltammograms has been described previously.<sup>10</sup> The peak voltammograms of the phenol (1h) obtained using the various reference electrodes were measured with a 0.048M-solution of the phenol in methanol containing LiClO<sub>4</sub> (0.3M). We found:  $E_p$ (s.c.e.–KCl) 1.05 V;  $E_p$ (s.c.e.–LiCl) 1.06 V;  $E_p$ (Ag wire) 0.98 V;  $E_p$ (Ag–Ag<sup>+</sup>) 0.45 V.

**Electrolyses. General.**—The phenol to be oxidised, the supporting electrolyte, and the buffer were dissolved in 60 ml [with electrode arrangements (a), (b), (c), (e), and (f)] or 40 ml [electrode arrangement (d)] of methanol or methanol–acetonitrile contained in the electrolysis cell. The electrolyses were carried out at constant potential (see Table 1) with a stirring rate of 4–5 revolutions s<sup>-1</sup> unless otherwise stated.

**Product Analysis.**—Phenols (1a), (1b), (1d), (1e), (1f), and (1h). After the electrolysis the electrolyte was poured into

phosphate buffer (pH 6—7) containing  $\text{CH}_2\text{Cl}_2$  (50 ml) with vigorous stirring. The  $\text{CH}_2\text{Cl}_2$  phase was separated. The aqueous phase was extracted a further four times with  $\text{CH}_2\text{Cl}_2$  (40 ml). The combined extracts were washed once with water, dried (sodium sulphate), and evaporated at reduced pressure. The n.m.r. internal, analytical standard

*Phenol* (1g). During electrolysis a brown precipitate formed which was filtered off and extracted with  $\text{CH}_2\text{Cl}_2$ . The  $\text{CH}_2\text{Cl}_2$ -insoluble residue was the diphenoquinone (12g). The  $\text{CH}_2\text{Cl}_2$ -soluble material was a mixture of the starting material, the quinone (13g), and polymers. Pure (13g) was obtained by extraction of the starting material and the

TABLE 6

Compounds isolated from the anodic oxidations of the phenols (1a—h); m.p.s and spectroscopic data

Compound	M.p.(°C)	Lit. m.p.	Ref. <sup>a</sup>	Spectral data
4-Methyl-4-methoxycyclohexa-2,5-dienone (2b)	63.5—64.0 (subl.)	62—63	14	Ref. 6 <sup>b</sup>
4-Methyl-2,4-dimethoxycyclohexa-2,5-dienone (2f)	111.5—112 (toluene)	110—111	15	Ref. 15 <sup>b</sup>
4,4-Dimethoxycyclohexa-2,5-dienone (2h)	Oil			Ref. 6 <sup>b</sup>
2,6-Dimethyl-4-methoxyphenol (3c)	77—78	77—77.5	20	
2,6-Di- <i>t</i> -butyl-4-methoxyphenol (3d)	104—105.5 (subl.)	106—107	16	
2,4,6-Trimethoxyphenol (3g)	63.5—64.0 (subl.)	66	26	$m/e$ 184 ( $M^+$ ); $\delta$ 3.73 (3 H, s), 3.83 (6 H, s), 5.13 (1 H, s), 6.17 (2 H, s)
Dimer of (4c)	141—141.5 (subl.)	134—135	17	Ref. 17 <sup>a</sup>
2,6-Di- <i>t</i> -butyl-2-methoxycyclohexa-3,5-dienone (4d)	Oil	<i>c</i>		$\nu_{\text{max.}}$ 3 060, 1 710, 1 670 $\text{cm}^{-1}$ ; $m/e$ 236 ( $M^+$ ); $\delta$ 0.92 (9 H, s), 1.21 (9 H, s), 3.07 (3 H, s), 6.3 (2 H, m), 6.7 (1 H, m)
Dimer of (4f)	133—135	133—135	15	Ref. 18 <sup>b</sup>
Dimer of (4g)	149.5—150 (subl.)	<i>c</i>		$\nu_{\text{max.}}$ (KBr) 1 750, 1 710, 1 640 $\text{cm}^{-1}$ ; $m/e$ 368 ( $M^+$ ); $\delta$ 2.95—3.70 (21 H, s), 3.11, 3.22, 3.39, 3.49, 3.55, 3.62 (3 H, s) (all OMe), 5.52 (1 H, d, $J$ 4 Hz), 5.81—6.37 (2 H, m)
4,4'-Dihydroxy-3,3',5,5'-tetramethylbiphenyl (6c)	218—219 (subl.)	226	18	Ref. 2 <sup>b</sup>
4,4'-Dihydroxy-3,3',5,5'-tetra- <i>t</i> -butylbiphenyl (6d)	183	185	19	
2,6-Dimethyl-4,4-dimethoxycyclohexa-2,5-dienone (8c)	Oil	<i>c</i>		$\nu_{\text{max.}}$ (film) 1 695, 1 665, 1 630 $\text{cm}^{-1}$ ; $m/e$ 182 ( $M^+$ ); $\delta$ 1.93 (6 H, s), 3.37 (6 H, s), 6.58 (2 H, s)
2,6-Di- <i>t</i> -butyl-4,4-dimethoxycyclohexa-2,5-dienone (8d)	Oil		27	$\nu_{\text{max.}}$ (film) 1 675, 1 650, 1 630 $\text{cm}^{-1}$ ; $m/e$ 266 ( $M^+$ ); $\delta$ 1.25 (18 H, s), 3.33 (6 H, s), 6.50 (2 H, s)
3,3',5,5'-Tetramethyldiphenoquinone (12c)	213—214	215	18	Ref. 2 <sup>b</sup>
3,3',5,5'-Tetra- <i>t</i> -butyldiphenoquinone (12d)	224—225 (subl.)	245—247	21	$\delta$ 1.37 (36 H, s), 7.73 (4 H, s)
3,3',5,5'-Tetramethoxydiphenoquinone (12g)			22	
2,6-Dimethyl- <i>p</i> -benzoquinone (13c)	71.5—74 (EtOH)	72—73	24	Ref. 2 <sup>b</sup>
2,6-Di- <i>t</i> -butyl- <i>p</i> -benzoquinone (13d)	67—68	67.5—68.5	23	
2,6-Dimethoxy- <i>p</i> -benzoquinone (13g)	253—254 (subl.)	251.5	24	$\delta$ ( $\text{CF}_3\text{CO}_2\text{H}$ ) 3.93 (6 H, s), 6.16 (2 H, s)
4-Methoxy-4-phenylcyclohexa-2,5-dienone (14)	92.5—93.0	91—93	25	

<sup>a</sup> Samples prepared as described in these references were used for identification of the electrolysis products. <sup>b</sup> The i.r., mass, and n.m.r. spectral data given in this reference are identical with those determined for the compound isolated in this study. <sup>c</sup> New compound.

[1,1,2-tetrabromoethane in oxidations of (1d) and nitromethane for all the others] was added to the residue and this was then dissolved in  $\text{CCl}_4$  or  $\text{CDCl}_3$ . The n.m.r. peaks were identified by comparison with the spectra of the pure compounds obtained as described below (in doubtful cases the pure compound was added as internal reference). Individual compounds were estimated quantitatively from the integrated n.m.r. spectra.

*Phenol* (1c). The diphenoquinone (12c) which precipitated during electrolysis was filtered off, dried, and weighed. The filtrate was analysed as described above.

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polymers from this residue with  $\text{CCl}_4$ . The filtrate was worked up and analysed as described above.

*Separation and purification of products.* The products actually isolated and purified are listed with m.p.s and spectroscopic data in Table 6.

The 4,4-dimethoxycyclohexa-2,5-dienones (8) are rapidly cleaved to the corresponding quinones in the presence of acid. Because of this instability it was very difficult to separate the products from electrolysis of phenols (1c) or (1d) by chromatography on silica gel or aluminium oxide (even basic grades failed). Silica gel or aluminium oxide chromatography can be used for separation and purification

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of the products from oxidation of the phenols (1a), (1b), and (1f). However, we found that chromatography on a Celite-activated carbon (1 : 1) column<sup>2</sup> with methanol as eluant is a generally useful method for separation of the products from anodic oxidation of the phenols (1a—h). The Celite-activated carbon column was washed with a phosphate buffer (pH 7) prior to use.

All the *ortho*-dienones [(4) and (11)] except (4d) underwent a Diels-Alder reaction<sup>17</sup> to give dimers during work-up. In the case of 2,2-dimethoxy-6-methoxycyclohexa-3,5-dienone (4g) the dimerisation reaction was so rapid that the monomer could not be detected by n.m.r. analysis run immediately after work-up. The only *ortho*-dienone isolated and characterised is (4d). The other *ortho*-dienones were isolated as their dimers (Table 6).

**Preparative oxidations. Phenol (1c).** The phenol (1c) (6.0 g, 0.049 mol) was dissolved in methanol (100 ml) containing *sym*-collidine (0.8 ml), benzene (12 ml), and LiClO<sub>4</sub> (4 g), and transferred to the electrolysis cell.<sup>2</sup> The anode was a hollow graphite cylinder (AUC graphite, internal diameter 31 mm, length 100 mm) and the cathode at first a tungsten wire (diameter 0.5 mm, length 100 mm) placed on the centre line of the anode. The electrolysis was carried out at -50 °C at constant potential (1.27 V relative to the Ag-Ag<sup>+</sup> reference). The initial current was 500 mA. When 3.6 F mol<sup>-1</sup> of current had been passed through the cell the electrolysis was interrupted and a small sample of the electrolyte was analysed directly by n.m.r. We found a product mixture consisting of (8c), (3c) (a small amount), and (4c) with a molar ratio between (3c) + (8c) and (4c) of *ca.* 2.6 : 1 (no starting material was detected by n.m.r.). In order to improve the [(3c) + (8c)] : (4c) ratio the tungsten cathode was replaced by a steel cathode (diameter 10 mm, length 100 mm) and the electrolysis was continued as above. When another 1.7 F mol<sup>-1</sup> had been passed through the cell the [(3c) + (8c)] : (4c) ratio had changed to *ca.* 7.6 : 1. However, the (3c) : (8c) ratio had increased. In order to diminish the (3c) : (8c) ratio the small tungsten cathode was reinserted into the cell and another 0.8 F mol<sup>-1</sup> was passed through the cell (this time at a temperature of -20 °C, otherwise as above). The electrolyte was poured into phosphate buffer (pH 7, 150 ml) with rapid stirring. Extraction with CH<sub>2</sub>Cl<sub>2</sub> (4 × 50 ml), drying (Na<sub>2</sub>SO<sub>4</sub>), and evaporation gave a mixture (n.m.r.) of (3c) (10%), (8c) (64%), and (4c) (12%). The mixture was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (50 ml), extracted with NaOH solution (2M, 3 × 15 ml), and stirred for 15 min with dilute H<sub>2</sub>SO<sub>4</sub> (2M; 3 × 15 ml), and stirred for 15 min with dilute H<sub>2</sub>SO<sub>4</sub> (2M; 15 ml). The CH<sub>2</sub>Cl<sub>2</sub> phase was separated and extracted with water (50 ml), phosphate buffer (pH 7, 50 ml), and water (50 ml). Evaporation gave a semi-solid residue (6.8 g) from which pure (13c), m.p. 71.5—74 °C [3.34 g, 50% yield based on (1c)] was obtained by recrystallisation from methanol at -40 °C.

**Phenol (1d). Attempt to optimise the yield of (4d).** The phenol (1d) (5.0 g), LiClO<sub>4</sub> (5 g), and NaHCO<sub>3</sub> (5 g) were dissolved/dispersed in methanol (500 ml) and transferred to the electrolysis cell (cylindrical vessel with a cooling mantle, and a lid with holes for the electrodes). The anode was platinum (the same as used in the analytical experiments, 50 cm<sup>2</sup>) and the cathode a nickel wire (diameter 3 mm, length 60 mm, area 5.7 cm<sup>2</sup>). The electrolysis was carried out at 10 °C and constant potential [2.2 V relative to the s.c.e.(LiCl) reference]. When 3.4 F mol<sup>-1</sup> of current had been passed through the cell the electrolysis was interrupted and the electrolyte was poured into a phosphate buffer (pH 7, 400 ml) with rapid stirring. Extraction with CH<sub>2</sub>Cl<sub>2</sub>, drying (Na<sub>2</sub>SO<sub>4</sub>), and evaporation gave 6.4 g of crude product. Chromatography on an activated carbon-Celite (1 : 1) column (200 g) with methanol as eluant gave (8d) (3.0 g, 47%), and a 1 : 3 mixture of (4d) and (8d) (1.11 g). Elution with CH<sub>2</sub>Cl<sub>2</sub>-hexane gave a mixture of (1d), (3d), (12d), and (13d) (1.36 g). Rechromatography of the 1 : 3 mixture of (4d) and (8d) with methanol as eluant gave a 3 : 1 mixture of (4d) and (8d) from which pure (4d) (0.05 g, 1%) was isolated by recrystallisation from light petroleum at -45 °C.

**Phenol (1d). Synthesis of (8d).** The phenol (1d) (10 g), LiClO<sub>4</sub> (4 g), and (-)-*sym*-collidine (1.0 ml) were dissolved in methanol (110 ml) and transferred to the electrolysis cell used in experiments 36—38 fitted with the hollow graphite anode (90 cm<sup>2</sup>) and a tungsten wire cathode (1.6 cm<sup>2</sup>). The electrolysis was carried out at 10 °C and constant potential [2.0 V relative to the s.c.e.(LiCl) reference]. When 5.6 F mol<sup>-1</sup> of current had been passed the electrolysis was interrupted and the electrolyte was worked up in the same way as in the former experiment, yield 10.0 g (77%) of pure (8d) (n.m.r.).

**p-Phenylphenol.** The phenol (3 g, 0.018 mol) and LiClO<sub>4</sub> (1 g) were dissolved in methanol (60 ml) and transferred to the electrolysis cell used in the analytical experiments fitted with the platinum anode (50 cm<sup>2</sup>) and a tungsten wire cathode (0.6 cm<sup>2</sup>). The oxidation was carried out at 10 °C and constant current (300 mA). When 4 F mol<sup>-1</sup> of current had been passed through the cell the electrolysis was interrupted, and the electrolyte was poured into a phosphate buffer (pH 7, 200 ml), and extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 × 50 ml). The CH<sub>2</sub>Cl<sub>2</sub> extract was washed with water, dried (Na<sub>2</sub>SO<sub>4</sub>), and evaporated to give 3.75 g of crude product. Filtration of this through alumina (60 g deactivated with 150 ml of wet ether; toluene as eluant) gave 3.73 g of product which on recrystallisation from toluene yielded pure (14), m.p. 91—92.5 °C (3.06 g, 87%).

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