Anodic Oxidation of Phenolic Compounds. Part III.[1] Anodic Hydroxylation of Phenols. A Simple General Synthesis of 4-Alkyl-4-hydroxycyclohexa-2,5-dienones from 4-Alkylphenols

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The oxidation of simple, monohydric phenols at a lead dioxide anode in aqueous sulphuric acid has been studied. The effects of current density, electrolysis time, pH, concentration of phenol, and method of anode preparation on conversion and product distribution have been investigated, and optimal conditions for anodic hydroxylation of simple phenols have been deduced. In all cases studied the hydroxy-group entered the 4-position: thus 4-substituted phenols gave 4-substituted 4-hydroxycyclohexa-2,5-dienones, and phenols without substituents at C-4 gave p-benzoquinones. The former reaction provides a simple and efficient synthesis of these cyclohexa-2,5-dienone derivatives. A mechanism involving hydrolysis of an anodically generated phenoxonium ion is suggested. Evidence is presented which indicates that the phenoxonium ion is formed by ' chemical ' oxidation with anodically generated lead dioxide. The lead dioxide anode is superior to carbon, nickel, and platinum anodes for hydroxylation.

WE have demonstrated previously [1] that 2,6-di-t-butyl-p-cresol and 2,4,6-tri-t-butylphenol, upon oxidation at a platinum anode in acetonitrile containing 0·1% of water, are converted in high yield into the corresponding 4-alkyl-4-hydroxycyclohexa-2,5-dienones via anodically generated phenoxonium ions. Similarly, 2,6-xylenol is oxidized in good yield to 2,6-dimethyl-p-benzoquinone.[2] These findings indicated that the hydrolysis of anodically generated phenoxonium ions might afford a general synthetic method for conversion of phenols into cyclohexa-2,5-dienones or hydroquinones. As hydroquinones and cyclohexa-2,5-dienones are valuable synthetic intermediates [3,4] and as no simple or general methods for the preparation of cyclohexa-2,5-dienones were available,[4] we decided to investigate the synthetic utility of the anodic hydroxylation reaction. As model compounds we chose p-cresol (I), o-cresol (II), 2,4-xylenol (III),
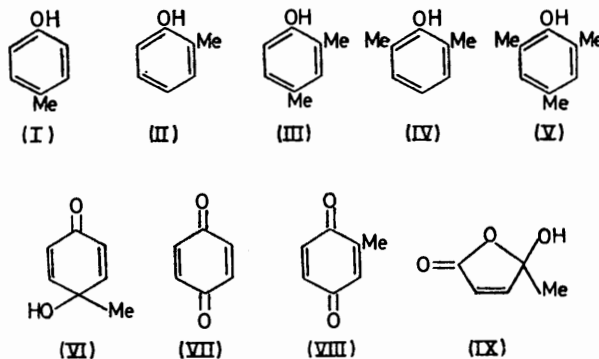
[1] Part II, A. Ronlán and V. D. Parker, *J. Chem. Soc. (C)*, 1971, 3214.
[2] A. Ronlán, *Chem. Comm.*, 1971, 1643.
[3] E. J. Corey, S. Barcza, and G. Klotman, *J. Amer. Chem. Soc.*, 1969, **91**, 2478.
[4] J. P. Loudon, *Progr. Org. Chem.*, 1961, **5**, 46.

2,6-xylenol (IV), and mesitol (V). Preliminary investigations showed that the best yields of hydroxylated products were generally obtained by electrolysis in aqueous M-sulphuric acid or, when the phenol was not sufficiently soluble, in a 7 : 1 mixture of acetonitrile and aqueous M-sulphuric acid. The present study is therefore limited to these solvents. The hydroxylation of phenol [5] and 2,4-xylenol [6] at a lead dioxide anode in aqueous sulphuric acid has also been studied in other laboratories and found to give hydroquinone (yield * 100%; conversion * 80%; current efficiency 35·4%) and 4-hydroxy-2,4-dimethylcyclohexa-2,5-dienone (yield 33%; conversion 72%; current efficiency 56%), respectively.

EXPERIMENTAL

[1]H N.m.r. spectra were recorded for solutions in CDCl$_3$ with Me$_4$Si as internal standard. For voltammetric measurements a polished, circular lead disc (area 0·17 cm^2) mounted in a Teflon holder was used. All lead anodes were polished mechanically prior to each experiment (these polished lead anodes are referred to as PLE). Several different pretreatments (preoxidation in pure M-H$_2$SO$_4$, cathodic reduction, etc.) of the lead anode were tried. Mechanically polished (the polishing was carried out with various grades of carborundum powder until a bright, smooth lead surface was obtained) oxide-free lead electrodes (PLE) gave the highest and more reproducible yields of hydroxylated products. The lead dioxide-on-carbon anode was prepared by anodic precipitation [7] of lead dioxide on a carbon rod [length × diam. ($h × \phi$) = 13 × 5 cm]. Potential sweep experiments were made with a P.A.R. 173/176 potentiostat, a linear sweep generator and an X/Y plotter. All potentials were measured against the standard calomel electrode (SCE). The galvanostat was an Amel model 555 instrument. Preparative and analytical electrolyses were carried out in open, water-cooled, cylindrical vessels with a hollow cylinder as anode † and a carbon rod as cathode. The diaphragms (when used) were Celloton grade VI porous cylinders.‡ The cell content was stirred magnetically and the temperature was kept at 10° by external cooling.

Anodic Oxidation of the Phenols (I)—(V). *Analytical Runs*.—The phenol was dissolved or dispersed in 160 ml of M-H$_2$SO$_4$ or MeCN–M-H$_2$SO$_4$ and electrolysed at constant current until the desired amount of current had passed. The anolyte was adjusted to pH 4 with solid potassium hydrogen carbonate and extracted continuously (42 h) with methylene chloride § (300 ml). The oil obtained on evaporation of the extract was analysed by quantitative [1]H n.m.r. with dioxan as internal analytical standard. The peaks due to the various compounds in the reaction mixture were identified by comparison with spectra of pure compounds obtained from the preparative experiments de-

scribed later. The molar ratio of the components in the reaction mixture was determined by integration and the absolute amounts were determined by comparison with the integral of the dioxan peak.¶ After extraction with methylene chloride the neutral aqueous solution was passed through anion- and cation-exchange resins, the resulting salt-free solution was evaporated, and the residue was analysed by [1]H n.m.r. (solvent D$_2$O, with dioxan as internal standard).

*Preparative Electrolysis.*** *Identification of Products.*—
p-*Cresol.* The electrolysis was carried out on a PLE with a diaphragm. The anode chamber was charged with p-cresol (13·5 g, 0·125 mol) dissolved in M-H$_2$SO$_4$ (1250 ml) and the cathode chamber with M-H$_2$SO$_4$ (300 ml). The electrolysis was carried out at a constant current density (D_A) of 1·38 A dm^{-2}. When an amount of current (Q) corresponding to 9·20 F mol^{-1} had been passed through the cell the electrolysis was interrupted and the anolyte transferred to a separating funnel. The electrolysis cell, the anode, and the outside of the diaphragm were washed with water (3 × 100 ml). The washings were combined with the anolyte and extracted with ether (1 × 100 and 4 × 50 ml). The extract was washed with M-H$_2$SO$_4$ (3 × 25 ml), dried (Na$_2$SO$_4$), and evaporated to yield an oil (1·5 g), which by quantitative [1]H n.m.r. was shown to consist of p-cresol †† (0·6 g), 4-hydroxy-4-methylcyclohexa-2,5-dienone (VI) (0·3 g), p-benzoquinone (VII) (0·5 g), m.p. 115—116°, and methyl-p-benzoquinone (VIII) (0·1 g), m.p. 68—69°.

The aqueous phase was worked up in two different ways: (i) by chromatography on a carbon–Celite column, or (ii) by continuous extraction with methylene chloride.

(i) The ether dissolved in the aqueous phase was removed under reduced pressure and the solution was then filtered through a carbon–Celite column ($h × \phi = 85 × 110$ mm) made by mixing activated carbon powder (100 g) and Celite (Johns Manville, Hyflo Supercel; 100 g). The column was eluted successively with water (500 ml), phosphate buffer (pH 6; 500 ml), water (300 ml), methanol (500 ml), and ether (2750 ml). Fractions (100 ml) were collected. Continuous extraction of fractions 6—14 (acidified to pH 2 with H$_2$SO$_4$) with ether (200 ml) for 20 h yielded, after evaporation, an oil (1·2 g), δ 1·73 (3H, s), 5·90 (1H, s), 6·10 (1H, d, J 5·7 Hz), and 6·30 (1H, d, J 5·7 Hz); $\nu_{max.}$ (CHCl$_3$) 1770 and 1710 cm^{-1}; m/e 114 (M^+). Sublimation of this oil in high vacuum at 85° gave a quantitative yield of a crystalline compound, m.p. 125—126°; δ 2·40 (3H, s), 6·68 (1H, d, J 16·1 Hz), and 7·20 (1H, d, J 16·1 Hz); $\nu_{max.}$ (Nujol) 1674 and 1630 cm^{-1}; m/e 114 (M^+). On the basis of these data and comparison with those reported [8] the oil was identified as 5-hydroxy-5-methylfuran-2-one (IX) and the crystals as trans-4-oxopent-2-enoic acid (X). Evaporation of fractions 19—33 gave crystals (7·8 g), m.p. 72—75°. Sublimation in high vacuum at 70° yielded colourless crystals (7·2 g), m.p.

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* Throughout this paper the term yield refers to the molar fraction of the *oxidized* starting material consisting of the specified compound, and the term conversion refers to the fraction of the starting material which has been oxidized. The molar fraction of the total starting material that has been converted to a specific compound is thus obtained by multiplying the yield by the conversion.

† $h × \phi = 13 × 5$ cm for analytical runs and 20 × 13 cm for preparative runs.

‡ In analytical runs with a diaphragm the volume of anolyte was 160 ml and that of catholyte 20 ml.

§ The methylene chloride was also used to rinse the cell and the anode.

¶ Calibration factors were obtained by carrying out the work-up procedure on mixtures of known composition.

** The experimental conditions were chosen on the basis of the results of the analytical runs.

†† The methyl absorption at δ 2·25 was used for quantitative determination.

[5] F. H. Cowitz, U.S.P. 3,509,039/1970 (*Chem. Abs.*, 1970, **73**, 115,824w).

[6] F. Fichter and J. Meyers, *Helv. Chim. Acta*, 1925, **9**, 74.

[7] Y. Shibasakai, *J. Electrochem. Soc.*, 1958, **105**, 624.

[8] R. Scheffold and P. Dubs, *Helv. Chim. Acta*, 1967, **79**, 798.

75—77°, δ 1·50 * (3H, s), 3·80 (1H, s), 6·15 (2H, d, J 10 Hz), and 6·96 (2H, d, J 10 Hz); $\nu_{max.}$ (KBr) 1678 and 1645 cm^{-1}; m/e 124 (M^+), identified from these data and comparison with an authentic sample [9] as 4-hydroxy-4-methylcyclohexa-2,5-dienone (VI) (yield 51%, conversion 96%).

(ii) The pH of the combined aqueous phases was adjusted to 4 with solid potassium hydrogen carbonate. The resulting solution was extracted continuously for 42 h with
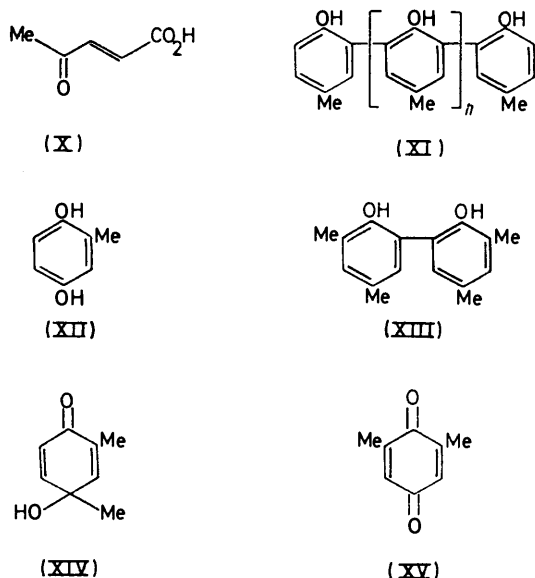
methylene chloride (500 ml). Evaporation yielded compound (VI) as brown crystals (8·1 g). Sublimation in high vacuum at 70° yielded white crystals (7·5 g), m.p. 75—77° (yield 51%).

Extraction of the lead anode with hot methylene chloride yielded, after evaporation, a black tar (1·7 g). The n.m.r. [δ 2·33 * (Me)] indicated that this was a mixture of coupling products (XI; n = 0, 1, 2, etc.). Acetylation of the tar followed by chromatography on silica gel (methylene chloride–ether, 20 : 1) gave the acetates of (XI) with n = 0 and 1.

o-Cresol. The electrolysis was carried out on o-cresol (13·5 g, 0·125 mol) as described for p-cresol (D_A 4·2 A dm^{-2}; Q 15 F mol^{-1}). The anolyte was extracted continuously with methylene chloride (500 ml) after neutralization but without prior extraction with ether. Evaporation yielded an oil (11·3 g) which after chromatography on silica gel (chloroform) yielded methyl-p-benzoquinone (VIII) (8·0 g), m.p. 67—68° (lit.,[10] 67—68°), δ 2·08 * (3H, d, J 1·5 Hz) and 6·74 (3H, m); o-cresol (1·3 g), δ 2·22 * (3H, s); and methylhydroquinone (XII) (1·4 g), m.p. 127—127·5° (lit.,[11] 124—125°), δ 2·15 *; yield of hydroxylated products [(VIII) + (XII)] 68%; conversion 90%. Extraction of the anode with hot methylene chloride yielded tars (1·4 g) which n.m.r. indicated to be coupling products of o-cresol.

2,4-Xylenol. The electrolysis was carried out on 2,4-xylenol (15·2 g, 0·125 mol) as described for p-cresol (D_A 3·80 A dm^{-2}; Q 4 F mol^{-1}). The anolyte was extracted with ether (3 × 100 ml). Evaporation of the extract yielded

* Peaks used for quantitative determination of the compound in mixtures are marked with an asterisk.

[9] E. Bamberger, Ber., 1903, **36**, 2028.
[10] R. Nietzki, Ber., 1877, **10**, 833.

an oil (4·6 g) which after chromatography on silica gel (200 g; benzene–ether, 5 : 1) yielded starting material (0·9 g), δ 2·23 *, and 2,2'-dihydroxy-3,3',5,5'-tetramethylbiphenyl (XIII) (2·8 g), m.p. 136—137° (lit.,[6] 137°); δ 2·30 *br (12H, s). The pH of the aqueous phase was adjusted to 4 with solid potassium hydrogen carbonate and the solution was extracted continuously (48 h) with methylene chloride (500 ml). Evaporation yielded a yellow, semisolid mass (9·0 g) which on recrystallization from water gave white crystals (8·2 g), m.p. 53—54°; 1·47 * (3H, s), 1·89 (3H, s), 4·80 (1H, s), 6·14 (1H, d, J 10 Hz), 6·71 (1H, m), and 6·91 (1H, q), identified as the monohydrate of 4-hydroxy-2,4-dimethylcyclohexa-2,5-dienone (XIV) by comparison with an authentic sample [9] (yield 44%; conversion 94%).

2,6-Xylenol. The electrolysis was carried out on 2,6-xylenol (15·3 g, 0·125 mol) as described for 2,4-xylenol (D_A 3·80 A dm^{-2}; Q 4 F mol^{-1}). The anolyte and the anode were extracted with methylene chloride (5 × 100 ml). The combined extract was washed with saturated potassium hydrogen carbonate and water, dried, and evaporated to yield an oil (14·0 g). Chromatography on silica gel (800 g; benzene–ether gradient) gave 2,6-dimethyl-p-benzoquinone (XV) (9·6 g), m.p. 70° (lit.,[12] 70°), δ 2·08 * (6H, d, J 2 Hz) and 6·61 (2H, m); 3,3',4,4'-tetramethyldiphenoquinone (XVI) (1·3 g), m.p. 213—214° (lit.,[12] 215°); and starting material (1·4 g), δ 2·28 * (6H, s) [yield of (XV) 62%; conversion 91%].

Mesitol. The electrolysis of mesitol (17·0 g, 0·125 mol) was carried out in MeCN–m-H₂SO₄ (D_A 2·32 A dm^{-2}; Q 2·6 F mol^{-1}). The pH of the anolyte was adjusted to 4 with solid potassium hydrogen carbonate and the solution was evaporated to dryness at reduced pressure. The residue was extracted with methylene chloride (5 × 100 ml). Evaporation of the extracts yielded a semisolid mass (16·1 g) which on recrystallization from ethanol–water yielded 4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dienone (XVII) (13·8 g), m.p. 45—46° (lit.,[13] 45·5—46°), δ 1·44 * (3H, s), 1·87 (6H, s), 3·52 (1H, s), and 6·68 (2H, s); and starting material (1·5 g), δ 2·24 * (9H, s) [yield (XVII) 81%; conversion 90%].
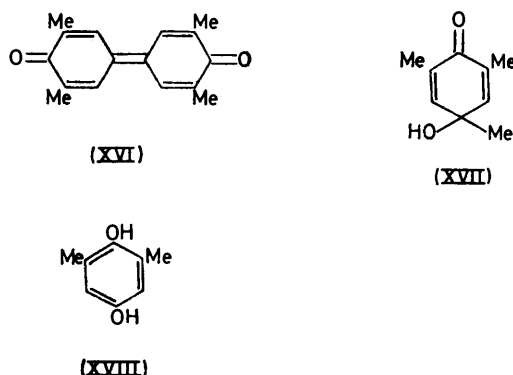
RESULTS

p-Cresol. The effect of various anode materials on the anodic hydroxylation of p-cresol in m-H₂SO₄ was studied. The results are given in Table 1. The effect of varying D_A and the p-cresol concentration on product composition was studied in detail and the results are shown in Tables 2

[11] R. Nietzki, Ber., 1877, **10**, 1935.
[12] R. G. R. Bacon and A. R. Izzat, J. Chem. Soc. (C), 1966, 791.
[13] E. Bamberger and A Rising, Annalen, 1901, **316**, 292.

and 3, respectively. The yield of (VI) was found to be strongly dependent on the pH of the electrolyte. At pH values below 2 the yield is as shown in Table 2. But at pH values above 2 the yield of (VI) is drastically reduced; instead coupling products (XI) are obtained.

o-Cresol, 2,4-xylenol, 2,6-xylenol, and mesitol. The dependence of product composition and conversion on D_A was

TABLE 1

Anodic hydroxylation of *p*-cresol in M-H$_2$SO$_4$ [a], effect of anode material

Anode material	D_A/ A dm^{-2}	Q/ F mol^{-1}	C * (%)	Yield of (VI) (%)	Yield of (XI) (%)
Lead (PLE)	2·3	15	85	40	16
PbO$_2$–C	4·4	15	85	41	15
Carbon	6·7	15	41	11	15
Platinum	2·3	230	66	0	28
Nickel	2·3	15	57	27	35
PbO$_2$–C	0 [b]	0 [b]	32	9	51

[a] 0·1M-Solutions of *p*-cresol. [b] The oxidation was carried out exactly as in the second experiment except that no current was passed through the freshly prepared PbO$_2$–C anode (this experiment represents a 'chemical' oxidation by electrochemically prepared lead dioxide).

* Conversion.

investigated for the phenols (II)—(V). The results are shown in Tables 4—7.

With 2,6-xylenol further experiments were carried out (in M-H$_2$SO$_4$ with a diaphragm) in which D_A was kept constant (6·25 A dm^{-1}) while Q was varied. The following relationship between Q, yield of hydroxylated products [(XV) + (XVIII)], and conversion was established [Q F mol^{-1}, (XV) + (XVIII) (%), conversion (%)] : [2·6, 53, 42], [7·5, 59, 42], [15·5, 58, 73], and [21·0, 37, 87].

TABLE 2

Anodic oxidation of *p*-cresol on PLE; product composition as a function of D_A

Electrolyte	D_A/A dm^{-2}	Conversion	Yield (%)	
			(VI)	(XI)
M-H$_2$SO$_4$ [a]	0·23	88	31	24
	0·78	93	53	18
	1·55	90	46	15
	2·23	85	41	15
	3·88	81	47	15
	6·20	73	50	12
M-H$_2$SO$_4$ [b]	0·78	82	39	14
	1·55	88	46	12
	2·32	82	57	12
	3·10	77	54	16
	3·88	77	41	12
MeCN–M-H$_2$SO$_4$ [c]	0·23	80	31	21
	0·78	72	36	24
	2·32	64	33	27

[a] No diaphragm; Q 13 F mol^{-1}. [b] Carried out with a diaphragm; Q 10 F mol^{-1}. [c] Carried out with a diaphragm; Q 2·6 F mol^{-1}.

TABLE 3

Anodic oxidation of *p*-cresol on PLE in M-H$_2$SO$_4$; effect of *p*-cresol concentration on product composition [a]

Concn. (M)	Conversion (%)	Yield (%)	
		(VI)	(XI)
0·05	56	55	8
0·1	93	52	14
0·5 [b]	92	26	43

[a] No diaphragm; Q 11 F mol^{-1} in all experiments; D_A 0·8 A dm^{-1}. [b] An additional 16% yield of unidentified products was obtained.

Using *o*-cresol and 2,4-xylenol a series of experiments were carried out in M-H$_2$SO$_4$ on the PLE with a diaphragm but the results of these experiments were very similar to those obtained without a diaphragm and are not included in Tables 3 and 4.

TABLE 4

Anodic oxidation of *o*-cresol on PLE; product composition as a function of D_A (electrolyte M-H$_2$SO$_4$) [a]

D_A/dm^{-2}	Conversion (%)	Yield (%)		
		(VIII)	(XII)	(VIII) + (XII)
1·55	90	40	13	53
3·88	82	45	13	57
6·20	82	42	16	58
9·30	71	47	13	60

[a] Carried out without a diaphragm; Q 12 F mol^{-1}.

TABLE 5

Anodic oxidation of 2,4-xylenol on PLE; product composition as a function of D_A

Electrolyte	D_A/A dm^{-2}	Conversion (%)	Yield (%)	
			(XIII)	(XIV)
M-H$_2$SO$_4$ [a]	0·78	91	27	14
	1·55	91	26	18
	2·32	90	25	23
	3·88	88	23	29
	6·20	88	22	27
MeCN–M-H$_2$SO$_4$ [b]	0·23	86	31	37
	0·78	90	30	34
	1·55	88	24	33
	3·88	71	27	40

[a] No diaphragm; Q 17 F mol^{-1}. [b] Carried out with a diaphragm; Q 2·6 F mol^{-1}.

TABLE 6

Anodic oxidation of 2,6-xylenol on PLE; composition as a function of D_A

Electrolyte	D_A/ A dm^{-2}	Conversion (%)	Yield (%)	
			(XV) + (XVIII)	(XVI)
M-H$_2$SO$_4$ [a]	0·78	88	47	10
	2·32	82	49	7
	6·20	43	51	
MeCN–M-H$_2$SO$_4$ [b]	0·23	67	38	36
	0·78	65	36	30
	2·32	64	33	16

[a] No diaphragm; Q 12 F mol^{-1}. [b] Carried out with a diaphragm; Q 2 F mol^{-1}.

TABLE 7

Anodic oxidation of mesitol on PLE; product composition as a function of D_A

Electrolyte	D_A/A dm^{-2}	Conversion (%)	Yield (%) of (XVII)
M-H$_2$SO$_4$ [a]	0·28	71	45
	1·55	52	48
	2·32	28	54
MeCN–M-H$_2$SO$_4$ [b]	0·23	85	64
	0·78	88	77
	1·55	89	76
	2·32	89	76

[a] No diaphragm; Q 14 F mol^{-1}. [b] Carried out with a diaphragm; Q 2·6 F mol^{-1}.

The oxidation of 2,4-xylenol, 2,6-xylenol, and mesitol on a platinum anode was also investigated. A comparison of the results of these investigations with the results of similar investigations on the PLE is shown in Table 8.

The anode potential of a rotating (300 rev. min⁻¹) lead dioxide disc * was measured as a function of D_A during electrolysis of a 0·1M-solution of p-cresol in M-H_2SO_4. At D_A 0·77 A dm⁻² the initial anode potential was 1·57 V. During the first 13 min of the electrolysis it increased linearly to 1·96 V and then remained constant for the rest of the electrolysis.† Above 1·62 A dm⁻² the potential of the PLE was independent of D_A and equal to 2·05 V (this potential was reached within 2 min after initiation of the electrolysis). At D_A 0·2 or 0·5 A dm⁻² the potential was not constant but varied periodically. The lowest potential measured was 1·27 V. From this value the potential rose graudually to 1·35 V in 2·5 min. At 1·35 V an increase to 1·63 V in

TABLE 8

Comparison of anodic oxidation of 2,4-xylenol (III), 2,6-xylenol (IV), and mesitol (V) on a platinum anode (Pt) and on the PLE ^{a}

Phenol	Anode	$D_A/$ A dm⁻²	$Q/$ F mol⁻¹	C * (%)	Hydroxyl- ation (%)	Coupling (%)
(III)	PLE	0·77	2·0	90	(XIV) (34)	(XIII) (30)
(III)	Pt	0·77	2·0	95	(XIV) (23)	(XIII) (23)
(IV)	PLE	0·77	2·0	65	(XV) (35)	(XVI) (30)
(IV)	Pt	0·77	2·0	71	(XV) (25)	(XVI) (44)
(V)	PLE	0·77	3·9	100	(XVII) (76), (XV) (12)	
(V)	Pt	0·77	3·9	79	(XVII) (27), (XV) (68)	
(V)	PLE	0·23	2·6	84	(XVII) (68), (XV) (15)	
(V)	Pt	0·23	2·6	54	(XVII) (12), (XV) (58)	

^{a} All experiments were carried out in MeCN–M-H_2SO_4 with a diaphragm.

* Conversion.

0·3 min followed by a decrease back to 1·27 V in 0·3 min set in, *etc.* The potential of the PLE as a function of D_A was also determined in pure M-H_2SO_4 and the following relationship between D_A and the potential ‡ (E) of the lead dioxide disc (or the PLE) was established (D_A/A dm⁻², E/V): (0·2, 1·80), (0·4, 1·83), (1·4, 1·90), (2·5, 1·95), (3·0, 1·97), and (6·0, 1·98).

Voltammograms were recorded with stationary and rotating PLEs and lead dioxide electrodes with the pure electrolytes and with 0·1M-solutions of the phenols (I)—(V). With anodic sweeping there was usually no appreciable current until above 1·50 V (sweep rate 10 mV s⁻¹). In the following cathodic scan a far larger *oxidation* (anodic) current was obtained with solutions that contained a phenol than with the pure solvents. Typical voltammograms are shown in Figures 1 and 2. The voltammograms (a) and (b) in Figure 1 were recorded with a rotating PLE, but cyclic voltammograms recorded on a stationary PLE in M-H_2SO_4 and in a 0·1M-solution of p-cresol in M-H_2SO_4 were almost identical with the voltammograms (a) and (b), respectively.§ The appearance of the voltammograms obtained on stationary and rotating PLEs is strongly dependent on scanning rate and the potential where the scan direction is reversed after the first anodic scan. Figure 2 shows the voltammograms obtained when the cycle ¶ is initiated at $E_i = 0$ V (dotted curve). The full drawn curve shows the *second*

* Prepared by anodic precipitation of lead dioxide on a platinum disc as described in ref. 7. Identical results were obtained on the PLE in stirred solutions.

† In all experiments the potential was monitored for 2·5 h.

‡ The potentials were reached within 2 min and remained constant during the rest of the electrolysis.

scan (the first followed the dotted curve) obtained when the scan is initiated at $E_i = 1·1$ V. At lower sweep rates the anodic peak (O₁) decreased and at sweep rates below 10 mV s⁻¹ this peak was not observed.
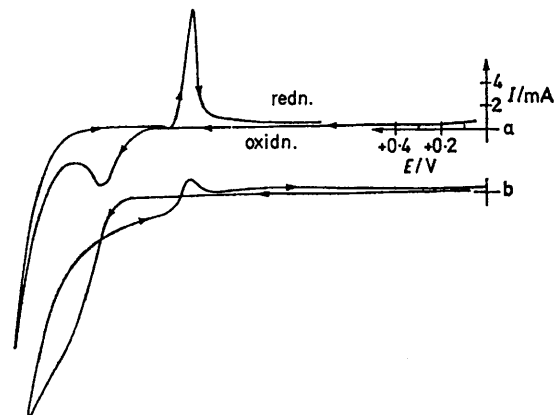

FIGURE 1   Voltammetry on a rotating PLE disc ($\omega^{1/2} = 15$); scan rate 10 mV s⁻¹ (direction of scan indicated by arrows); (a) in pure M-sulphuric acid; (b) in 0·1M-solution of p-cresol in M-sulphuric acid. The scan was initiated at $E = 0$ V, and the cathodic scan initiated (at 2·1 V) was recorded immediately after the anodic scan
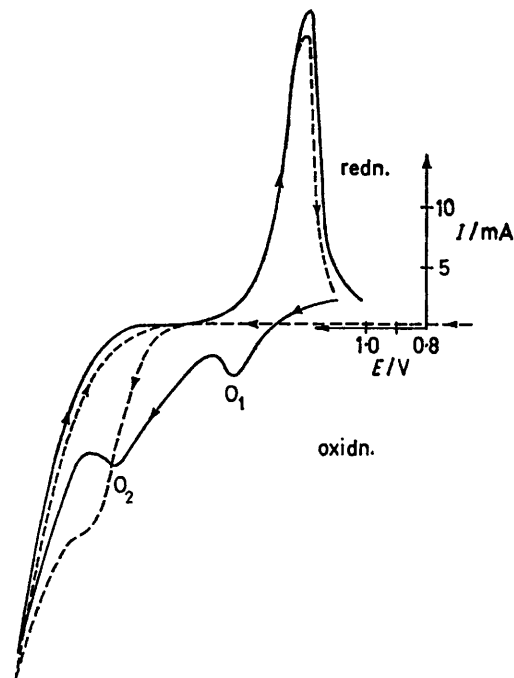

FIGURE 2   Fast sweep voltammetry on a rotating ($\omega^{1/2} = 15$) PLE in M-sulphuric acid (sweep rate 100 mV s⁻¹); (– – – –) scan initiated at $E_t = 0$ V; (———) second voltammogram obtained when the scan was initiated at E_t 1·1 V (direction of scan indicated by arrows)

Conditions for the best yields of hydroxylated phenols obtained in the preparative experiments are shown in Table 9.

§ With a stationery PLE the oxidation current obtained in the cathodic scan was slightly smaller than with a rotating PLE. It was also more erratic owing to the formation of gas bubbles on the anode surface.

¶ In one cycle the potential was varied linearly from E_t to 2·15 V and back to E_t.

TABLE 9

Yields of preparative scale hydroxylations of phenols
(I)—(V)

Phenol	$D_A/$ A dm⁻²	$Q/$ F mol⁻¹	Con-version (%)	E/V	Hydroxyl-ation yield (%)
p-Cresol [a]	1·38	9·2	96	2·05	(VI) (50)
o-Cresol [a]	4·20	15·0	90	2·12	(VIII) (68)
2,4-Xylenol [a]	3·80	4·0	94	2·09	(XIV) (44)
2,6-Xylenol [a]	1·55	4·0	91	2·08	(XV) (62)
Mesitol [b]	2·32	2·6	90	2·19	(XVII) (81)

[a] Carried out with 0·125 mol of the phenol in M-H₂SO₄.
[b] Carried out with 0·125 mol of the phenol in MeCN–M-H₂SO₄.

DISCUSSION

The electrode potential (E) for the reaction * $PbO_2 + SO_4^{2-} + 4H^+ + 4e = PbSO_4 + 2H_2O$ is $1·687 - 0·1182pH + 0·0295 \log a_{SO_4^{2-}}$ (vs. the normal hydrogen electrode).[14] Accordingly the lead dioxide electrode cannot be stable below 1·4 V (vs. SCE) in M-H₂SO₄. The potential measurements during electrolysis taken together with the results in Tables 3—7 and 9 show that the most successful hydroxylations are carried out at a potential well above 1·4 V. This means that the PLE is covered with a layer of lead dioxide and that it is equivalent to a freshly prepared lead dioxide electrode. This makes possible three oxidation pathways for the anodic oxidation of phenols on the PLE in sulphuric acid: †

(a) The oxidation occurs via direct charge transfer (c.t.) from the phenol to the lead dioxide anode which acts like a chemically inert electron acceptor.

(b) The oxidation occurs via an electrocatalytic oxidation, that is, the phenol is oxidized chemically by lead dioxide on the anode surface and the reduced lead species thus formed is oxidized (via c.t.) rapidly back to Pb^IV as it is part of the anode itself.

(c) The oxidation occurs via a combination of paths (a) and (b). The large difference in product composition (Table 1) between the chemical oxidation with lead dioxide and the electrochemical oxidations does not exclude oxidation via pathway (b), as the rapid reoxidation of reduced lead species (like PbO, Pb²⁺, or Pb₃O₄) formed in a chemical oxidation might make further oxidation of the radical cation or radical [(XIX) and (XX) in Scheme 1] formed in a normal chemical oxidation by lead dioxide [15] more favourable than the usual dimerization.‡ In some respects, oxidation via path (b)

resembles a constant-potential electrolysis on a chemically inert anode.

In order to gain further insight into the mechanism of charge transfer a series of voltammetric experiments were carried out. The rapid scan voltammograms (Figure 2) clearly show that the reduction of lead dioxide to lead sulphate proceeds through an unstable intermediate (e.g. Pb²⁺, Pb₃O₄, or PbO, which are hydrolysed in acidic solution) that is oxidized at a lower potential (O_1 in Figure 2) than lead sulphate (O_2 in Figure 2). Figure 1 shows that the addition of p-cresol (the same result was obtained with the other phenols) gives rise to a large oxidation current (curve b). As this oxidation current does not occur in pure M-H₂SO₄ (curve a), the oxidation current rise can be ascribed to oxidation of p-cresol. The reduction of lead dioxide by p-cresol may be assumed to proceed via the same kind of intermediate as the electrochemical reduction (Figure 2), an intermediate which is oxidized in the potential range between point A (1·50 V) and 1·38 V where the electrochemical reduction of lead dioxide sets in. We therefore cannot decide from these data whether the observed oxidation current is due to oxidation via path (a), or (b), or (c). However, since the oxidation current between 1·50 and 1·38 V is independent of the rotation rate of the PLE, an electrocatalytic mechanism [path (b) or (c)] is the most likely. The absence of any dependence on the rotation speed of the PLE could also be explained by assuming that the c.t. from the phenol to the lead dioxide anode is slow,§ but our previous investigations of the anodic oxidation of phenols [1,2] and extensive investigation of the lead dioxide anode [14] give us no reason to believe that this should be the case.

The potential measurements during electrolysis also indicate that the anodic oxidation follows path (b) or (c).¶ In pure M-H₂SO₄ the potential of the PLE is 1·8 V when $D_A = 0·2$ A dm⁻², i.e., the lead dioxide layer is perfectly stable and oxidation probably takes place via c.t. [path (a)]. In presence of p-cresol the potential drops to ca. 1·3 V, which means that the lead dioxide layer is no longer stable and that oxidation by c.t. [path (a)] is excluded. Most likely a dynamic situation is established on the PLE in which the reduced lead species formed by reduction of lead dioxide by p-cresol is oxidized back to lead dioxide [the reduced lead species is oxidized at a lower potential than lead sulphate; for example the potential (E_0) for the reaction Pb²⁺ + 2H₂O = PbO₂ + 4H⁺ + 2e is 1·18 V]. However, some

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* This is the dominant reaction of discharge (and charge in the other direction) in the pH region we have studied (ref. 14).

† It has been shown [14] that lead in higher oxidation states than IV does not occur on a lead anode.

‡ The fact that hydroxylated products are formed in the chemical oxidation of phenols by PbO₂ in M-H₂SO₄ (Table 1) shows that PbO₂ is capable of oxidizing phenoxyl radicals or radical cations to phenoxonium ions (see ref. 2), but as this is not the case with the reduced lead species, two different PbO₂ systems must react with the same phenol molecule in order to generate a phenoxonium ion. This explains why the radical combination reaction dominates in the chemical oxidation by PbO₂. In the electrocatalytic process (b) the same PbO₂ molecule can carry out both oxidations because of the rapid re-oxidation.

§ In an anodic oxidation proceeding via rapid c.t. (the normal case) the diffusion layer on the stationary PLE is depleted of phenol (especially when the oxidation as here with the PLE is carried out at a potential well above the oxidation potential of the phenol) which means that no oxidation current due to oxidation of the phenol should be observed during the cathodic scan in fast sweep cyclic voltammetry.

¶ The combination pathway c must be oxidation by PbO₂ followed by c.t. oxidation of the radical cation or radical thus formed.

[14] J. P. Carr and N. A. Hampson, Chem. Rev., 1972, 72, 689.
[15] W. I. Taylor and A. R. Battersby, 'Oxidative Coupling of Phenols,' Marcel Dekker, New York, 1967, pp. 4—51.

of the reduced lead species reacts with sulphate ions to form lead sulphate (the voltammogram in Figure 2 clearly shows that the reduced lead species is short-lived), which is not oxidized at 1·3 V. Consequently the anode surface is slowly passivated by lead sulphate and eventually the potential rises to 1·63 V where the lead sulphate is oxidized to lead dioxide and the anode surface is reactivated (and the potential drops to 1·27 V).

chemical oxidation by lead dioxide and the overall oxidation *via* path (*b*) or path (*c*).

No exact coulometric data are available for the anodic oxidation of phenols on the PLE, as the oxidations are always accompanied by oxidation of water and corrosion of the lead dioxide layer. But the high yields of hydroxylated products obtained and the results of our previous study [1,2] suggest that the anodic hydroxylation of
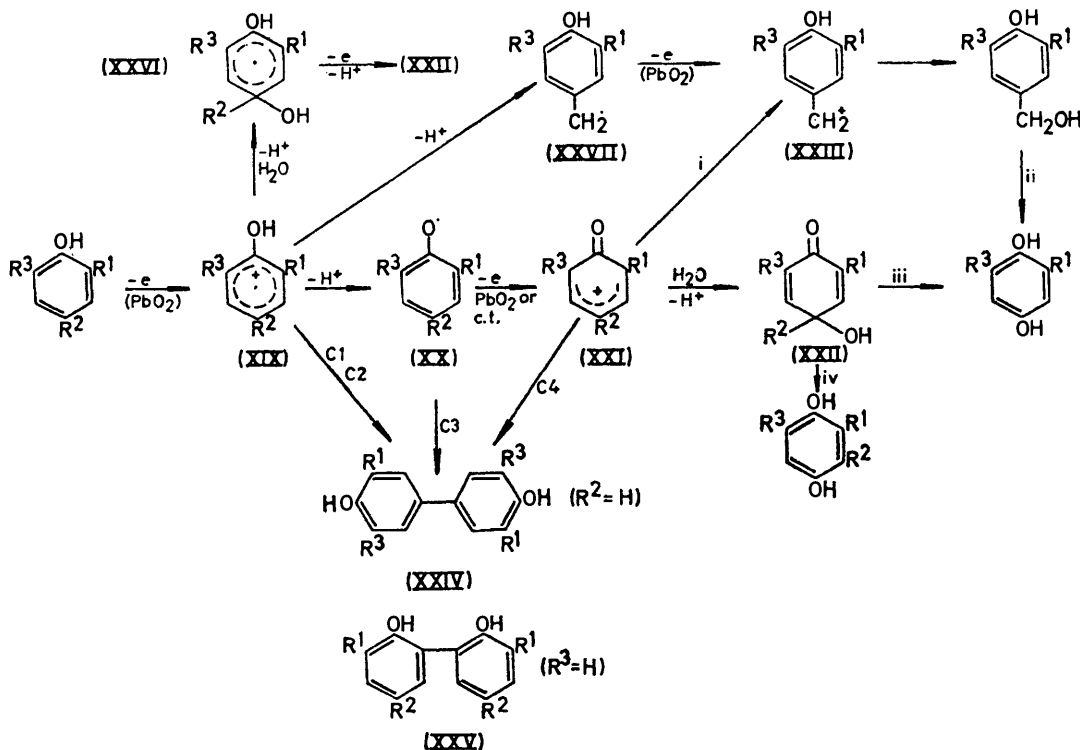
SCHEME 1 C1, nucleophilic attack of the starting phenol to form a dimeric radical cation followed by further oxidation and deprotonation; C2, dimerization of the radical cation followed by deprotonation and aromatization; C3, dimerization of the radical followed by aromatization; C4, nucleophilic attack of the starting phenol on the phenoxonium ion followed by deprotonation and aromatization. i, Acid-catalysed rearrangement of the phenoxonium ion (see ref. 1); ii, further anodic oxidation (see ref. 19); iii, aromatization ($R^2 = H$); iv, dienone–phenol rearrangement. The symbol —e(PbO₂) refers to chemical oxidation by PbO_2 and the symbol —e(c.t.) to oxidation *via* direct charge transfer from the phenol to a chemically inert anode surface

The rate of c.t. to the anode decreases exponentially with decreasing anode potential, whereas the rate of chemical oxidation by lead dioxide remains constant, that is, at a sufficiently low potential, dimerization of the radical or radical cation formed by chemical oxidation of the phenol by lead dioxide is faster than further oxidation. This means that the product composition obtained in anodic oxidations at low potential should be similar to that obtained by chemical oxidation with lead dioxide. Our investigation (Tables 2, 4, and 5) shows that this is the case.*

On the basis of these arguments we conclude that the initial oxidation of phenols on the PLE proceeds *via*

* In Fichter's investigations (ref. 16) the anodic oxidation of simple phenols in M-H₂SO₄ on a lead dioxide anode gave dimeric and polymeric products almost exclusively. These experiments were carried out at low D_A (0·25 A/dm²) but also with high concentrations of the phenols (2M) which means that we cannot ascribe the high yields of coupled products to the low D_A alone.

phenols on the PLE in M-H₂SO₄ involves an anodically generated phenoxonium ion as shown in Scheme 1. According to this mechanism the coupling products encountered in the oxidation of the phenols (I)—(IV) could have been formed *via* four different coupling reactions (C1—4). Coupling reaction C1 involves nucleophilic attack of the starting phenol on the radical cation (XIX) generated by lead dioxide oxidation. If this mechanism were of any importance we should expect the oxidation of phenols with oxidants like ferric chloride or lead dioxide in M-H₂SO₄ to give predominantly hydroxylated products [*via* the intermediate (XXVI)], since water is a much better nucleophile than phenols and is present in massive excess. By the same kind of argument we can exclude coupling or hydroxylation by reactions involving nucleophilic attack of neutral molecules on the radical (XX). Little is known about the

[16] F. Fichter, ' Organische Electrochemie,' Theodor Steinkopf, Dresden, 1942, p. 109.

reactivity of radical cations such as (XIX). We can expect that they will be strong acids * and that deprotonation to the radical (XX) will be very fast, but since the rate of the dimerization (C2) is unknown, even if this reaction is possible, we cannot decide the relative importance of coupling reactions C2 or C3.†

If the coupled products are formed by reaction C2 or C3 the proportion of these products in the electrolysis mixture should be unaffected by the concentration of the starting phenol as long as D_A is kept constant, since the concentration of the intermediates (XIX) and (XX) is determined solely by D_A ‡ and the rate of formation of coupled products via reactions C2 or C3 is determined by the concentrations of (XIX) or (XX) alone. However, the results in Table 2 show that the proportion of coupling products in the electrolysis mixture is strongly dependent on the concentration of the phenol. This dependence is exactly what is expected if the coupled products are formed via reaction C4 § involving nucleophilic attack of the starting phenol on the anodically generated phenoxonium ion (XXI). Consequently it is likely that the coupled products encountered in our experiments are formed mainly via reaction C4. As mentioned before it is possible that reactions C2 or C3 are the main product-forming reactions at low D_A (<0.1 A dm^{-2}).

Hydroxylation occurred only in the 4-position of the starting phenol, as in our previous [1] study. However, in the anodic oxidation of p-cresol and 2,4-xylenol we have suggested that the phenoxonium ion (XXI; $R^1 = R^3 = H$, $R^2 = Me$, and $R^1 = R^2 = Me$, $R^3 = H$) reacts in the 2-position to give an ortho-coupled product [(XI) and (XIII)]. In a previous study of the reaction of phenol with the phenoxonium ion derived from 2,6-di-t-butyl-p-cresol we showed that the nucleophilic attack of the phenol occurred in the 4-position of the phenol to give 4-hydroxy-4-methyl-2,6-di-t-butylcyclohexa-2,5-dienone. Steric hindrance may well cause the phenoxonium ion derived from p-cresol or 2,4-xylenol to react with the phenols to give ortho,ortho-coupled products.

The cyclohexa-2,5-dienones (VI), (XIV), and (XVII) themselves are electrochemically active. At the cathode they are reduced back to the starting phenols, which to some extent explains the lower current efficiency when the oxidations are carried out without a diaphragm. At the anode one of the double bonds in the cyclohexa-2,5-dienone is cleaved oxidatively. This reaction was

studied in detail with (VI). Electrolysis of a $0.1M$-solution of (VI) in M-H_2SO_4 on a PLE showed that the lactone (IX) formed during anodic oxidation of p-cresol is an anodic oxidation product of (VI). A possible mechanism for this oxidation is outlined in Scheme 2. Attempts to carry out the anodic hydroxylation on a platinum anode ¶ in M-H_2SO_4 or in MeCN–M-H_2SO_4

SCHEME 2
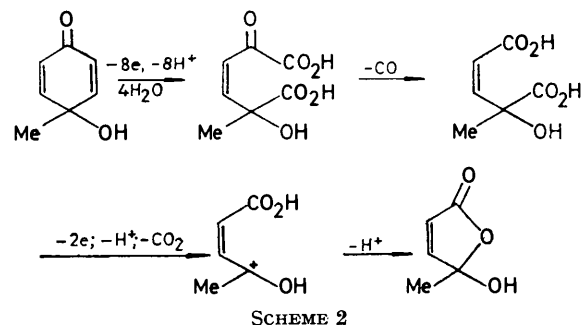
were unsuccessful (Tables 1 and 8). With o- and p-cresol and 2,4-xylenol the anode surface immediately became passivated owing to formation of a polymeric film and even at very low D_A (0.01 A dm^{-2}) the potential (at constant D_A) rapidly rose above 3.0 V.** With 2,6-xylenol a higher yield of the coupled product (XVI) was obtained on a platinum anode than on the PLE (Table 8). With mesitol more side-chain oxidation occurred on platinum than on the PLE (Table 8). Since the platinum anode acts like a chemically inert electron acceptor it is reasonable to assume that the oxidation of phenols follows the same mechanistic pathway here as in oxidations on the PLE (Scheme 1 with all oxidations as pure charge-transfer reactions). The higher yields of coupled products and the more extensive side-chain oxidation (mesitol) obtained on the platinum anode as compared with the PLE, might depend on differences in adsorption energies on platinum oxide and lead dioxide for the phenols and the intermediates (XIX) and (XX). On the lead dioxide surface of the PLE the intermediates (XIX), (XX), and (XXI) will probably be bound to the surface and not present as free species. Thus further oxidation [via oxidation by lead dioxide, pathway (b), or via c.t., pathway (c)] will be facilitated (the intermediates are in effect a part of the anode). The dimerization reaction (C2 or C3) will be inhibited, at least at low substrate concentration, by the lack of mobility of (XIX) or (XX). On the platinum oxide anode the intermediates (XIX)—(XXI) will not be adsorbed to the same extent, which means that they will be free to

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* The pK of the radical cations derived from monohydric phenols [17] is ca. -5.

† It has been argued [18] that phenoxyl radicals (XX) will not dimerize in acidic solution but disproportionate according to the equation: $2ArO\cdot + H_3O^+ = ArO^+ + ArOH + H_2O$. However even in acidic, aqueous solution, chemical oxidation of phenols (with for example PbO_2 or $FeCl_3$) gives predominantly dimerized products. This means that phenoxonium ions are not formed as free species to any appreciable extent as hydroxylated products should dominate in that case. It is reasonable to assume that the coupling reaction C3 is the preferred reaction of (XX) even in M-H_2SO_4.

‡ As the temperature was the same in all experiments we need not consider changes in the relative rate constants for the reactions C2 and C3.

§ Previously (ref. 2) we have demonstrated that this kind of coupling reaction is indeed possible.

¶ The platinum surface is covered with platinum oxide (approx. composition $PtO_{2.66}$) which means that the platinum anode is actually a platinum oxide anode.

** Similarly, cyclic voltammetry on stationary or rotating platinum discs in a $0.1M$-solution of p-cresol in M-H_2SO_4 showed a drastic reduction in the oxidation current between the first and the second anodic scans.

[17] E. J. Land, G. Porter, and E. Strachan, *Trans. Faraday Soc.*, 1961, **57**, 1885.

[18] W. A. Waters, *J. Chem. Soc.* (*B*), 1971, 2026.

[19] N. P. Neuriter, *J. Org. Chem.*, 1963, **28**, 3486.

dimerize [(XIX) and (XX)] or to rearrange [(XXI) to (XXIII)] in the usual manner. The difference in the results obtained on a platinum anode and on nickel and carbon anodes (Table 1) * can be explained in a similar way. The product (XV) from side-chain oxidation of (V) could be formed *via* the intermediate (XXVII) (Scheme 1). But this reaction involves cleavage of a carbon–hydrogen bond, which must be far slower † than cleavage of the oxygen–hydrogen bond leading to the radical (XX). Furthermore no bibenzyl or stilbene-quinone [formed by dimerization of (XXVII)] was detected in the oxidation of (V) on platinum and little side-chain oxidation occurs on the PLE. We therefore

* The formation in the anodic oxidation on carbon anodes of carboxylic acids [20] of products derived from carbonium ions and on platinum anodes of dimers derived from radicals (Kolbe reaction) can be rationalized in the same way.

† In our investigations (A. Ronlán and V. D. Parker, *Chem. Comm.*, 1970, 1567; A. Ronlán, J. Coleman, O. Hammerich, and V. D. Parker, submitted for publication) of the anodic oxidation of phenol methyl ethers we have shown that the deprotonation of radical cations or dications obtained from anodic oxidation of these ethers (cleavage of a carbon–hydrogen bond) is indeed very slow in comparison with deprotonation of radical cations obtained by anodic oxidation of phenols (cleavage of an oxygen–hydrogen bond).

think that this reaction sequence is only of minor importance. Results similar to those in Table 9 were obtained with derivatives of phenol where one or more of the carbon-bound hydrogen atoms were substituted with an alkyl, aryl, alkoxy-, or aryloxy-group.

It is generally believed [21] that hydroxylation of aromatic substrates in biological systems involves electrophilic attack of a hydroxyl radical or an oxygen–metalloenzyme complex formed by reduction of oxygen in the air. However, recently [22] the glucoside of (VI) was isolated from natural sources (*Cornus* species) indicating that hydrolysis of phenoxonium ions formed by oxidation of phenols may be of biological importance.

[20] L. Eberson in 'Chemistry of the Carboxyl Group,' ed. S. Patai, Interscience, New York, 1969, ch. 2.
[21] D. I. Metelitsa, *Russ. Chem. Rev.*, 1971, **40**, 563.
[22] S. Rosendahl Jensen, A. Kjaer, and B. Juhl Jensen, *Acta Chem. Scand.*, 1973, **27**, 367.