Anodic Pyridination of 2-Hydroxy-3-methoxy-5-methylbenzaldehyde and its Schiff's Base Derivatives

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Anodic oxidation of substituted phenols, 2-hydroxy-3-methoxy-5-methylbenzaldehyde (1) and its Schiff's base derivatives (2) in acetonitrile containing an excess of pyridine gave pyridinated phenols. Pyridination occurred at the methyl group of the hydroxybenzaldehyde (1) and the Schiff's base (2g) derived from *p*-nitroaniline, while for the other Schiff's base derivatives of (1) studied the pyridinium group was on the ring *meta* to the hydroxy and *ortho* to the imino group. The pyridination process was investigated by cyclic voltammetry and controlled potential and constant current electrolysis of (1), (2), and related phenols including 2-hydroxy-3-methoxybenzaldehyde Schiff's bases (4). Two different routes are suggested for pyridination, a process involving a phenoxonium ion and one involving a quinone methide. Under the conditions of controlled potential electrolysis, ring pyridination proceeds through the phenoxonium ion route and side-chain pyridination through the quinone methide route. The role of the imino group in the anodic oxidation of the phenolic Schiff's bases (2) and (4) is discussed. The principal mode is suggested to be catalysis of the dimerisation of the corresponding cation radicals by accepting the proton of the hydroxy-group intramolecularly to remove the positive charge from the reaction centre.

In the anodic oxidation of Schiff's bases (4) derived from 2-hydroxy-3-methoxybenzaldehyde (3), the formation of the cation radical salts (20) from the ring-coupled dimers (19) (Schiff's bases of 4,4′-dihydroxy-5,5′-dimethoxybiphenyl-3,3′-dicarbaldehyde) and of the protonated Schiff's bases have been reported (*cf.* Scheme 3).[1] A mechanism involving coupling of the cation radicals of (4) has been proposed on the grounds that (20) is formed almost quantitatively upon electrolysis of (4) in the presence of excess of pyridine and on electrolysis of the dimeric Schiff's bases (19). A nucleophilic attack of the unoxidised molecule of (4) on the corresponding cation radical or on the phenoxonium ion has been discarded, though the possibility of dimerisation of neutral phenoxyl radicals derived from (4) to give (19) could not be excluded. Since anodic dimerisation of simple phenols has been suggested to involve coupling of the phenoxyl radicals [2–6] and/or attack of the starting phenol on the phenoxonium ion,[6] coupling of the cation radicals of (4), if this is the case, must be due to intramolecular hydrogen bonding in the molecule. Studies on the Schiff's bases (2) derived from 2-hydroxy-3-methoxy-5-methylbenzaldehyde (1), which have a methyl group on the ring *para* to the hydroxy group, were expected to afford further information on the mechanism of the formation of the cation radical salts (20) from (4). Controlled potential electrolysis of the hydroxybenzaldehyde (1) and its Schiff's bases (2) in acetonitrile containing an excess of pyridine gave pyridinated phenols in which the pyridinium group was *meta* to the hydroxy group except for (1) and (2g) derived from *p*-nitroaniline.[7]

This paper reports the results of cyclic voltammetry and macroscale electrolysis of (1), (2), and the related phenols (3)—(8) in acetonitrile in the presence and absence of various nucleophilic reagents. The effect of the imino group in the phenolic Schiff's bases (2) and (4) on the follow-up reactions are discussed. Products (9)—(20) were obtained upon electrolysis under the various conditions.

RESULTS

Cyclic Voltammetry.—In acetonitrile containing 0.1M-sodium perchlorate, the phenolic Schiff's base (2) showed two anodic peaks and three cathodic peaks in the voltage sweep range 0—1.5 V *versus* s.c.e.† A typical voltammogram of the Schiff's base (2d) derived from t-butylamine is shown in Figure 1a. The cathodic peak at the lowest positive potential increased with an increase in the voltage sweep rate while the other cathodic peaks decreased. No cathodic peak was observed when the voltage sweep was limited to the potential of the first anodic peak. Thus the cathodic peaks can be ascribed to the reduction of species formed at the second anodic peak. However, the nature of the cathodic peaks was not studied further because no

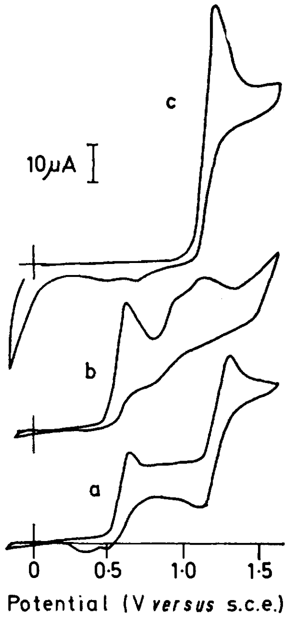

Figure 1 Cyclic voltammograms of the phenolic Schiff's base (2d) (2.0mM) in acetonitrile containing 0.1M-$NaClO_4$ (a) without added acid or base, (b) with pyridine (8mM), (c) with sulphuric acid (8mM) at a glassy carbon electrode (area, 0.071 cm^2): voltage sweep rate, 50 mV s^{-1}

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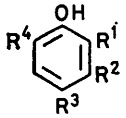
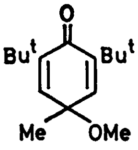
† Some of the phenolic Schiff's bases (2) showed one or two more anodic peaks at higher potentials, but these were not studied further.

stable product was obtained on controlled potential electrolysis of (2) at the potential of the second anodic peak.

The effect of added acids and bases on the cyclic voltammetry of (2) was examined. Typical examples are illustrated in Figures 1b and c. In the presence of perchloric or sulphuric acid the first anodic peak decreased while the second peak increased. In the presence of excess of acid (Figure 1c) the first peak completely disappeared. The weaker acid, pyridinium perchlorate, had no appreciable effect on the voltammetry, indicating that pyridine is a



	R^1	R^2	R^3	R^4
(1)	CHO	H	Me	OMe
(2)	CH:NR	H	Me	OMe
(3)	CHO	H	H	OMe
(4)	CH:NR	H	H	OMe
(5)	CH$_2$NHBu^t	H	Me	OMe
(6)	CH$_2$NHBu^t	H	H	OMe
(7)	Bu^t	H	Me	Bu^t
(8)	Me	H	H	Me
(9)	CH:NR	1-pyridinium,ClO$_4^-$	Me	OMe
(10)	CH:NR	imidazol-1-yl	Me	OMe
(11)	CH:NR	benzimidazol-1-yl	Me	OMe
(12)	CHO	H	CH$_2$-1-pyridinium,ClO$_4^-$	OMe
(13g)	CH:N-4-NO$_2$C$_6$H$_4$	H	CH$_2$-1-pyridinium,ClO$_4^-$	OMe
(14)	CHO	1-pyridinium,ClO$_4^-$	Me	OMe
(15)	Bu^t	H	CH$_2$-1-pyridinium,ClO$_4^-$	Bu^t
(16)	Bu^t	H	CH$_2$OMe	Bu^t



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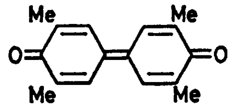

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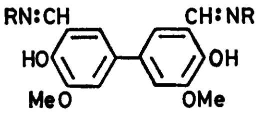

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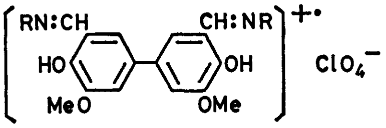


(20)

a; R=Me
b; R=Et
c; R=Pr^i
d; R=Bu^t
e; R=Ph
f; R=4-OMeC$_6$H$_4$
g; R=4-NO$_2$C$_6$H$_4$

stronger base than the Schiff's bases (2). When pyridine was present the first peak increased and the second peak decreased. With excess of pyridine (Figure 1b) the second peak disappeared and a small ill-defined peak appeared between the original first and second peaks. Similar results were obtained with added imidazole or benzimidazole. Results of cyclic voltammetry of (2) and other phenols are summarised in Table 1.

Cyclic voltammetry of phenoxide ions derived from 4-alkyl-2,6-di-t-butylphenols in acetonitrile has been reported by Evans *et al.* and voltammetric peaks due to the oxidation of phenoxyl radicals have been identified.[8] Figure 2 shows typical voltammograms of four phenols under similar conditions. 2,6-Di-t-butylcresol (7) gave essentially the same voltammogram as observed by the above authors.[8] Thus the anodic peak at 0.50 and 0.54 V in the voltammograms of (7) and (2d), respectively, are attributable to the oxidation of the corresponding phenoxyl radicals (Figures 2a and b). In the case of the hydroxybenzaldehyde (1) and its Schiff's base (2g) derived from *p*-nitroaniline, however, the corresponding peaks were not observed (Figures 2c and d). Pertinent peak potentials are summarised in Table 2.

TABLE 1

Results of cyclic voltammetry of the phenolic Schiff's bases (2) and related phenols [a]

Phenol	(E_{p1}	i_p/C) [b]	(E_{p1}Py	i_p/C) [c]	(E_{p1}Im	i_p/C) [d]	(E_{p1}BzIm	i_p/C) [e]	E_{p2} [f]	(E_pH$^+$	i_p/C) [g]
(2a)	0.63	10.9	0.61	18.3	0.56	18.9	0.61	17.8	1.15	1.03	37.9
(2b)	0.63	11.4	0.62	18.9	0.55	19.4	0.60	17.6	1.15	1.04	39.3
(2c)	0.67	11.2	0.63	17.8	0.57	21.2	0.63	17.8	1.15	1.06	33.5
(2d)	0.66	11.2	0.61	19.2	0.57	20.1	0.61	18.9	1.15	1.03	37.2
	(0.70	9.5) [h]	(0.72	14.4) [h]	(0.25	12.0) [i]			(0.97) [h]	(0.98	44.8) [h]
(2e)	0.78	10.7	0.66	24.3	0.58	21.4	0.66	16.5	1.16	1.10	47.9
(2f)	0.78	11.4	0.73	18.1	0.57	22.5	0.73	21.2	1.17	1.09	48.8
(2g)	0.88	10.0	0.60	28.9	0.55	30.1	0.61	28.5	1.17	1.18	40.1
(1)	1.13 [j]	33.7	0.66	28.1	0.58	28.9	0.61	28.5	*k*	1.14	42.3
(3)	1.20	35.0	0.85	23.4					*k*	1.20	42.4
(4d)	0.72	16.7	0.73	33.0					1.28	1.20	33.9
(4g)	1.03	16.3	0.87	25.2					1.53	1.26	35.7
(5)	0.33	12.5	0.33	12.5					1.10	0.95	30.1
(6)	0.47	15.2	0.46	15.8					1.36	1.12	33.0
(7)	1.10	32.6	1.10	23.4					*k*		
(8)	1.15	53.3	0.75	13.6					*k*		

[a] In acetonitrile containing 0.1M-NaClO$_4$ at a glassy carbon electrode (geometric area, 0.071 cm^2); concentration of phenol, 1.80—2.50mM; at 50 mV s^{-1}. Peak potentials are in V *versus* s.c.e. and peak currents in μA/mM. [b] The first anodic peak in the absence of added base. [c] In the presence of 7.2—10mM-pyridine. The peak current did not increase with further increase in the amount of base. [d] In the presence of 8mM-imidazole. [e] In the presence of 8mM-benzimidazole. [f] The second anodic peak in the absence of added base. [g] The anodic peak in the presence of 10mM-perchloric acid. [h] In methanol containing 0.1M-NaClO$_4$. [i] In methanol containing 8mM-sodium methoxide and 0.1M-NaClO$_4$. [j] The peak potential seems sensitive to small amounts of water contaminating the medium. [k] The second anodic peak was absent.

TABLE 2

Voltammetric peak potentials of phenoxide ions derived from (1), (2), and (7) [a]

Phenol	E_{p1}' [b]	E_{p2}' [c]	E_{p3}' [d]
(1)	0.10	1.13 [e]	
(2c)	0.01	0.55	0.80
(2d)	−0.14	0.54	0.75
(2e)	−0.08	0.38	0.83
(2f)	0.05	0.55	0.94
(2g)	0.05	1.00 [e]	
(7)	−0.46	0.50	0.98

[a] In acetonitrile containing 2.2mM-Me$_4$NOH and 0.1M-Et$_4$NClO$_4$ at a glassy carbon electrode (geometric area, 0.077 cm^2); concentration of phenol, 2.0mM; at 100 mV s^{-1}. [b] First anodic peak. [c] Second anodic peak. [d] Third anodic peak: the nature of the peak for (7) has been discussed (ref. 8). [e] The second anodic peak probably merged in the third anodic peak.

Figure 3 illustrates typical examples of the effects of voltage sweep rate on the first anodic peak current of various phenols in acetonitrile in the absence and presence of pyridine. E.c.e. character was suggested,[9] except for the voltammetry of (2) in the absence of pyridine (Figures 3b and c). For phenols with an imino group [(2) and (4)], the peak current in the presence of pyridine was enhanced compared to that in the absence of pyridine (Figures 3a—c: see also Figure 1 and Table 1). Conversely, for the phenols without an imino group the peak current in the absence of pyridine was larger (Figures 3d—f).

Controlled Potential Electrolysis.—Table 3 summarises typical results of controlled potential electrolysis of various phenols in acetonitrile with added bases. Hydrolysis of the ring-pyridinated Schiff's base (9) in aqueous hydrochloric acid gave the corresponding hydroxybenzaldehyde (14). On electrolysis of 2,6-xylenol (8) in the presence of pyridine, no substituted product was obtained, but 3,3′,5,5′-tetramethyldiphenoquinone (18) was isolated. Details of the procedures and identification of the products are described in the Experimental section.

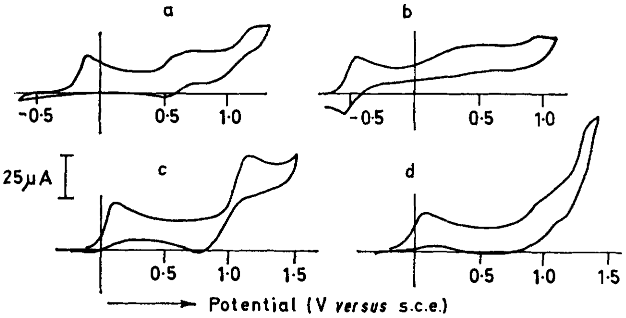


FIGURE 2 Cyclic voltammograms of (a) the phenolic Schiff's base (2d) (1.98mM), (b) 2,6-di-t-butylcresol (7) (1.99mM), (c) the hydroxybenzaldehyde (1) (2.07mM), and (d) the phenolic Schiff's base (2g) (2.04mM) in acetonitrile containing 0.1M-Et$_4$NClO$_4$ and 2.2mM-Me$_4$NOH at a glassy carbon electrode (area, 0.071 cm^2): voltage sweep rate, 100 mV s^{-1}

Electrolysis of the phenolic Schiff's base (2) in acetonitrile without added base at the potential of the first anodic peak gave a coulometric n value of 0.8—0.9. Except for the recovery of the starting Schiff's base as its protonated form (*ca.* 50%, see Experimental section), the products were intractable tars and attempts to characterise their nature were unsuccessful. With *N*-(2-hydroxy-3-methoxy-5-methylbenzyl)-t-butylamine (5) and *N*-(2-hydroxy-3-methoxybenzyl)-t-butylamine (6) severe electrode filming prevented electrolysis both in the presence and absence of bases.

TABLE 3

Results of controlled potential electrolysis of various phenols [a]

Phenol [amount/mmol]	Added base [b] (amount/mmol)	Applied potential [c]	n Value	Product isolated [yield (%)]
(2c) [0.66]	Py (6.25)	0.60	2.00	(9c) [72]
[0.74]	Im (3.7)	0.55	2.11	(10c) [73] [d]
[0.62]	BzIm (3.0)	0.65	1.97	(11c) [63] [d]
(2d) [0.43]	Py (6.25)	0.60	2.00	(9d) [75]
[0.58]	Im (2.9)	0.55	2.00	(10d) [71] [d]
[0.85] [e]	BzIm (4.25)	0.65	1.90	(11d) [65] [d]
(2e) [0.62]	Py (6.25)	0.65	2.03	(9e) [62]
(2f) [0.59]	Py (6.25)	0.70	1.98	(9f) [60]
(2g) [0.65]	Py (6.25)	0.65	(1.90) [f]	(13g) [31] [g]
(1) [0.61]	Py (6.25)	0.60	1.98	(12) [83]
(7) [0.62]	Py (6.25)	1.00	1.90	(15) [74]
(4d) [0.53] [e]	None	0.80	0.75	(20d) [47] [h]
[0.18] [e]	Py (0.20)	0.80	1.60	(20d) [100]
(4g) [0.32]	None	1.00	0.90	(20g) [33] [h]
[0.043] [i]	Py (0.064)	0.85	(1.65) [f]	None [j]
(8) [1.98]	Py (6.25)	0.70	1.95	(18) [79]

[a] In acetonitrile (50 ml) containing 0.1M-NaClO$_4$ at a glassy carbon plate anode; at room temperature [b] Py, pyridine; Im, imidazole; BzIm, benzimidazole. [c] V *versus* s.c.e. [d] Estimated by liquid chromatography (see Experimental section). [e] In 100 ml of acetonitrile. [f] The electrolysis did not go to completion and was stopped at this stage. [g] No other stable product was obtained but tarry material. [h] Theoretical yield is 50%.[1] [i] In 25 ml of acetonitrile. [j] Only tarry material was obtained.

Constant Current Electrolysis.—As seen in Table 3, controlled potential electrolysis of phenols (1) and (7) without an imino group gave side-chain pyridinated phenols as the main products. Parker and Ronlān have reported that constant current electrolysis of di-t-butylcresol (7) at a platinum electrode in acetonitrile containing methanol gives a ring methoxylated dienone (17) as the major product.[10] Essentially the same method was tried in an attempt to obtain ring-pyridinated product from (1) and (7): reticulated glassy carbon was used as the anode instead of platinum. Electrolysis of (7) in acetonitrile containing methanol gave the dienone (17) and the corresponding side-chain methoxylated phenol (16) in a ratio of 12.5 : 1 inconsistent with the results reported (17.6 : 1).[10] On electrolysis of (1) and (7) in the presence of pyridine, however, the side-chain pyridinated phenols (12) and (15), respectively, were the sole products isolated (Table 4).

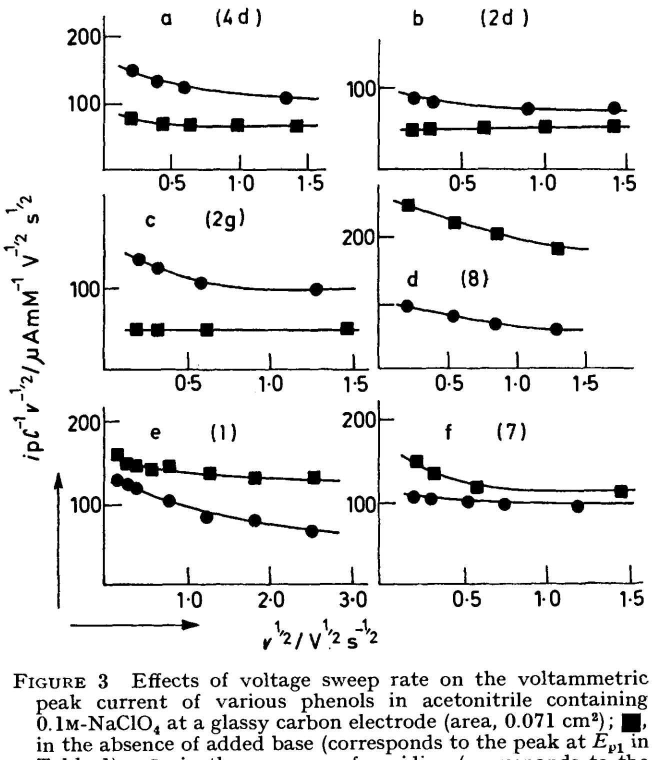
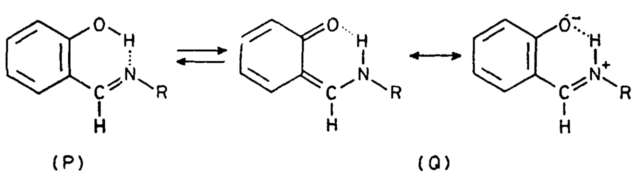


FIGURE 3 Effects of voltage sweep rate on the voltammetric peak current of various phenols in acetonitrile containing 0.1M-NaClO$_4$ at a glassy carbon electrode (area, 0.071 cm^2); ■, in the absence of added base (corresponds to the peak at E_{p1} in Table 1); ●, in the presence of pyridine (corresponds to the peak at E_{p1}Py); concentration of phenol, 1.5—2.5mM; concentration of pyridine, 6—10mM

DISCUSSION

The tautomeric equilibria of salicylaldehyde Schiff's bases between the phenol-imine (P) and quinone-amine (Q) forms have been shown to depend on the nature of the medium,[11,12] *e.g.*, in cyclohexane exclusively the (P) form, in water exclusively the (Q) form, and in ethanol both forms are present, but the (P) form predominates.



The absorption spectra of the phenolic Schiff's bases (2d) and (4d) in cyclohexane and in acetonitrile are closely related to those of *N*-ethylsalicylideneimine in cyclohexane and ethanol,[11] respectively, indicating that the relative amount of the (Q) form is small (*ca.* 10%) for (2) and (4) in the present solvent system. It is difficult, however, to state which form is preferentially oxidised at the electrode; in what follows the argument will be based on the (P) form, but essentially the same conclusion is reached from that based on the (Q) form.

Among the phenolic Schiff's bases (2) examined, those derived from aliphatic amines were oxidised more easily than those derived from aromatic amines (Table 1, E_{p1}) as observed for the other phenolic Schiff's base series (4).[1] These results are consistent with the view that the first anodic peak involves an electron transfer from the aromatic π-system including the hydroxy group rather than from the lone-pair of electrons on the nitrogen atom, that is, oxidation of a phenol takes place.[1] The second anodic peak of (2) (E_{p2}) can be ascribed to further oxidation of the cation radical of (2) mixed with the oxidation of the protonated form of (2), because the latter species was formed on electrolysis of (2) at the potential of the first peak and its peak potential (E_pH^+) is very close to E_{p2} (Table 1).

The mechanism of the anodic pyridination of phenols in the present study is summarised by Scheme 1.

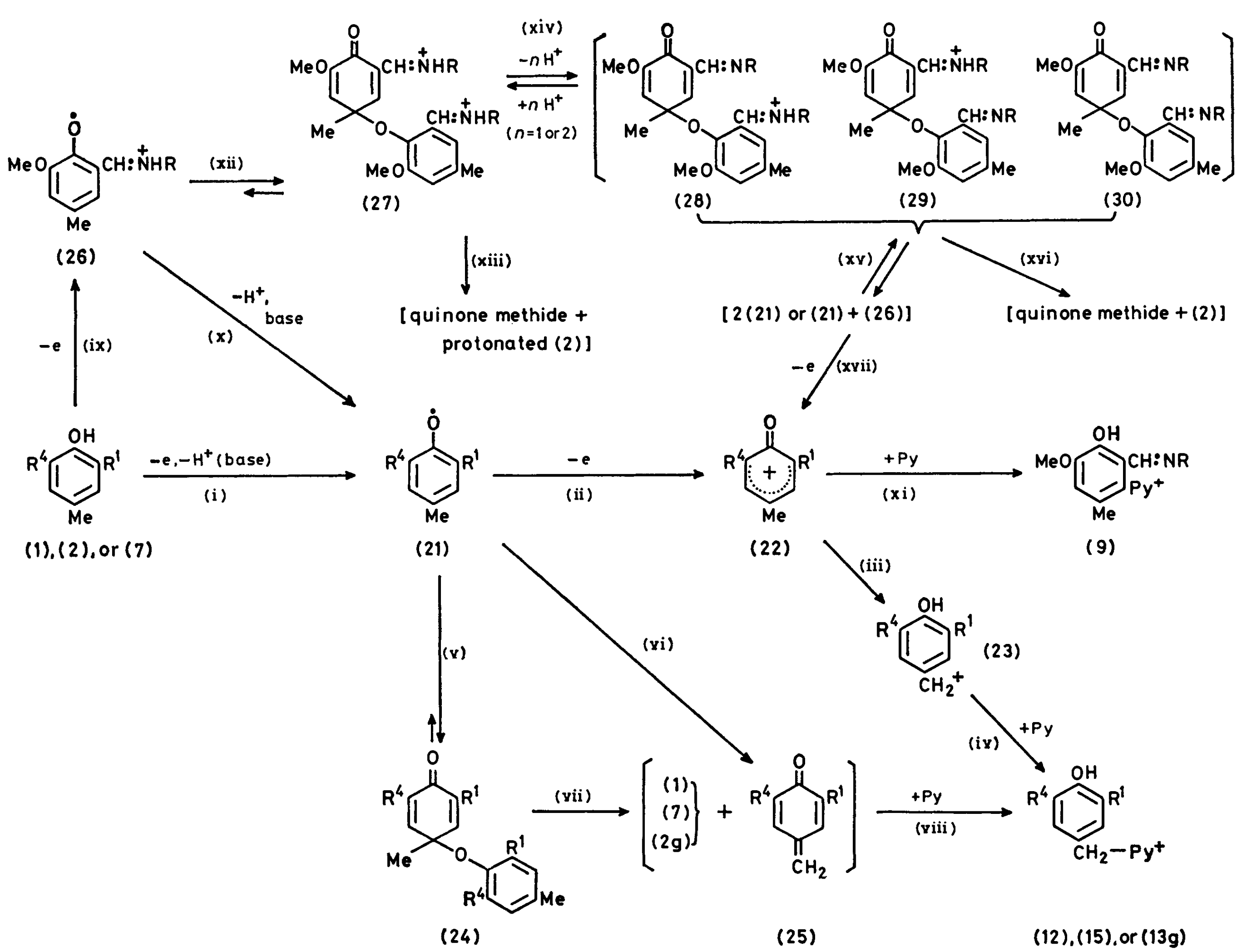
TABLE 4

Results of constant current electrolysis of phenols (1) and (7) [a]

Phenol [amount/mmol]	Solvent [b]	Added base [c] (amount/mmol)	Amount of current/mA	Anode potential (V *versus* s.c.e.)	Product isolated [yield (%)] [d]
(1) [1.19]	MeCN	Py (6.25)	200	~1.2	(12) [75]
[0.47]	MeCN	Py (6.25)	360	~1.5	(12) [54]
[0.50]	MeCN	MeOH (25)	200	~1.2	*e*
(7) [0.48]	MeCN	Py (6.25)	200	~1.2	(15) [72]
[0.53]	MeOH	Py (6.25)	200	~1.2	(15) [43] [f]
[0.97]	MeCN	MeOH (25)	200	~1.2	(16) [75], (17) [6]

[a] At a reticulated glassy carbon anode (8.38 cm^3; area *ca.* 226 cm^2). [b] 50 ml. [c] Py, pyridine. [d] Based on the amount of the substrate consumed. [e] A polymethoxylated product was isolated, but the structure is not yet clear. [f] No other stable product was isolated.

In unbuffered acetonitrile, anodic oxidation of simple phenols has been shown to give the corresponding phenoxonium ion probably through an e.c.e. mechanism:[2,8,10,13,14] deprotonation of the initially formed cation radical is assumed to be very fast. Since the voltammetric peak potential of di-t-butylcresol (7) in the presence of pyridine (E_{p1}Py) is higher than that of



SCHEME 1 Py = pyridine

the corresponding phenoxyl radical (21; $R^1 = R^4 = Bu^t$) (0.5 V, Figure 2b), electrolysis of (7) at $E_{p1}Py$ will give the phenoxonium ion (22) from which the side-chain pyridinated phenol (15) will be formed. Thus, the pyridination of (7) can be represented by steps (i)—(iv) in Scheme 1. It is not clear whether the attack of pyridine takes place on the cationic intermediate (22) or (23), though side-chain substitution of (7) (hydroxylation, methoxylation, and acetoxylation) has been suggested to involve (23).[6,10] Another pyridination mechanism, though it seems inconsistent with the voltammetric observation (Figure 2b), must be considered for (7), and this will be discussed later.

The peak potentials of the phenols without an imino or an amino group on the side-chain [(1), (3), and (8)] shifted in the cathodic direction by 500—700 mV when pyridine was added, except for that of (7) (see E_{p1} and $E_{p1}Py$ in Table 1). The large cathodic shift can be attributed to partial deprotonation of the phenols *via* hydrogen bonding to pyridine. In the case of (7), the lower acidity of the phenol and steric hindrance to the hydrogen bonding may be responsible for the low sensitivity of the peak potential to added pyridine. In the cyclic voltammetry of the phenoxide ion derived from (1) (Figure 2c), no peak due to the oxidation or the reduction of the corresponding phenoxyl radical (21; $R^1 = CHO$, $R^4 = OMe$) was discernible, indicating that the hydroxybenzaldehyde (1) is not oxidised to the phenoxonium ion (22) at the potential at which controlled potential electrolysis in the presence of pyridine was carried out (0.6 V), but the phenoxyl radical (21) undergoes rapid change to give some species electrochemically inactive in the potential range (—0.5—1 V). In the one-electron oxidation of di-t-butylcresol (7), either chemical[15,16] or electrochemical,[8b] the resulting phenoxyl radical (21) dimerises reversibly to the corresponding quinol ether (24): the equilibrium lies well towards (24).[16]

Disproportionation of (21) or decomposition of (24) affords the quinone methide (25) and the starting phenol, which is a relatively slow reaction.[8b,16] By assuming similar quinol ether formation for the oxidation of the hydroxybenzaldehyde (1) in the presence of pyridine, the process of anodic pyridination of (1) under the conditions of controlled potential electrolysis is represented by either of the sequences involving the corresponding quinone methide (25) in Scheme 1 [steps (i)–(v)–(vii)–(viii) or (i)–(v)–(vi)–(viii)]. A reaction of the quinone methide derived from (7) with methanol has been reported to give the benzyl methyl ether (16).[15,17] A similar reaction of (25) from (1) with pyridine seems reasonable. The regenerated starting phenol in steps (vi) or (vii) will be oxidised again, and the coulometric *n* value will eventually become 2 (Table 3).

The effects of voltage sweep rate on the peak current of (1) (Figure 3e) support the steps suggested above. Thus in the presence of pyridine, the rate of steps (vi) or (vii) competes with the sweep rate, and the peak current decreases to that of one-electron oxidation with the increase in the sweep rate.* The small decrease in the peak current of (7) in the presence of pyridine (Figure 3f) may indicate a partial contribution of the steps involving the quinone methide (25) (QM route) in addition to those involving the phenoxonium ion (22) (PO^+ route).

Constant current electrolysis of (7) in acetonitrile containing methanol gave the dienone (17) as the main product (Table 4), indicating that the corresponding phenoxonium ion (22) is actually formed under the conditions.[10] On electrolysis in the presence of pyridine, however, the side-chain-pyridinated phenol (15) was the sole product isolated, even though the current density and the anode potential were essentially the same as those in the methoxylation and the yields of products were comparable in both electrolyses. Similar results were obtained in the electrolysis of the hydroxybenzaldehyde (1), that is, the anode potentials (*ca.* 1.2 and *ca.* 1.5 V) were those expected for two-electron oxidation to take place in unbuffered acetonitrile but the side-chain-pyridinated phenol (12) was the main product. These results suggest that attack of pyridine on the phenoxonium ion (22) derived from (1) and (7) occurs preferentially at the side-chain. In the hexacyanoferrate oxidation of (7), however, a change in mechanism from the PO^+ to the QM route has been demonstrated when the system changes from highly to less acidic.[17]

Since electrolysis in acetonitrile containing methanol can be regarded as being carried out under acidic conditions because a proton is liberated and that in acetonitrile containing pyridine as being carried out under basic conditions, the possibility that methoxylation proceeds through the PO^+ route and pyridination through the QM route is not rigorously ruled out. Anodic pyridination of 2,4,6-tri-t-butylphenol under more basic conditions [MeCN–pyridine (1 : 1); controlled potential electrolysis] has been shown to give 2- and 4-pyridinated products,[18] which must be derived from the corresponding phenoxonium ion. This evidence cannot be a conclusive support for the PO^+ route in the case of 2,4-di-t-butylcresol (7), because a quinol ether such as (24) from 2,4,6-tri-t-butylphenol is not known and the corresponding quinone methide will not be formed from the phenoxyl radical derived from the phenol. Thus, for the formation of (12) under constant current conditions and that of (15) under both constant current and controlled potential conditions, it is hard to show which of the two routes is actually operative. However, we prefer the PO^+ route because the phenolic Schiff's bases (2) gave pyridinated products *via* the corresponding phenoxonium ion (22; $R^1 = CH{:}NR$, $R^4 = OMe$) under similar conditions. The possibility that in the presence of pyridine the phenoxonium ions (22) derived from (1)

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* The curved plot of $i_p/Cv^{1/2}$ against the sweep rate for (1) in the absence of pyridine probably represents the follow-up reactions of the corresponding phenoxonium ion (22) with water unavoidably contaminating the medium to give species electroactive at the potential. Similar follow-up reactions can be responsible for the curved plots in the absence of pyridine for phenols (7) and (8) (Figures 3d and f). Reactions of the phenoxonium ions derived from 4-alkyl-2,6-di-t-butylphenols have been reported.[8]

and (7) are deprotonated to give the quinone methides (25), which in turn are pyridinated to give (12) and (15), may also be considered. At the present stage, however, no conclusive support for such a process has been obtained.

The voltammetric peaks of the phenolic Schiff's bases (2) and (4) appeared at considerably less anodic potentials compared with those of the original hydroxybenzaldehydes (1) and (3) (Table 1, $E_{\mathrm{p}1}$). The potential difference is probably ascribed to partial deprotonation of (2) and (4) *via* intramolecular hydrogen bonding. Similar hydrogen bonding has been reported to affect the cathodic reduction of salicylaldehyde Schiff's bases.[19] Consequently, the structure of the cation radical derived from (2) seems best represented as (26) in Scheme 1.

The value of peak current for (2) in acetonitrile without added base suggests that the peak corresponds to a one-electron oxidation. The stoicheiometry of the process in the time-scale of cyclic voltammetry can be represented either by equation (1) or (2), where SH^+ denotes the protonated form of the Schiff's base (2).

$$2(2) \longrightarrow (22;\ \mathrm{R}^1 = \mathrm{CH{:}NR},\ \mathrm{R}^4 = \mathrm{OMe}) + \mathrm{SH}^+ + 2\mathrm{e} \qquad (1)$$

$$(2) \longrightarrow (26) + \mathrm{e} \qquad (2)$$

Equation (1) is based on the fact that SH^+ was formed on controlled potential electrolysis of (2) in acetonitrile without added base. Detailed steps involved in equation (1) would be one-electron transfer from (2) to give the cation radical (26), proton transfer between (26) and (2) to give the corresponding phenoxyl radical (21) and SH^+, and further one-electron transfer from (21) to give the phenoxonium ion (22). In this case, the proton transfer should be fast enough to result in a constant $i_\mathrm{p}/Cv^{1/2}$ value for the corresponding peak over the voltage sweep rate examined (Figure 3b). Since the ability of the phenolic Schiff's base (2) to accept a proton intermolecularly is smaller than that of pyridine (see Results section, effect of acids and bases on voltammetry), proton transfer from the cation radical (26) to pyridine must be faster than that to (2). Thus, if equation (1) were really the case, the peak current of (2) in the presence of pyridine would be twice as large as that in the absence of pyridine and the value of $i_\mathrm{p}/Cv^{1/2}$ for the peak would be constant over the voltage sweep rate examined. The results obtained on (2d) (Figure 3b) are incompatible with these expectations. The intermolecular proton transfer between the phenolic Schiff's base (2) and its cation radical (26) is not so fast as to make the first anodic peak of (2) totally irreversible.

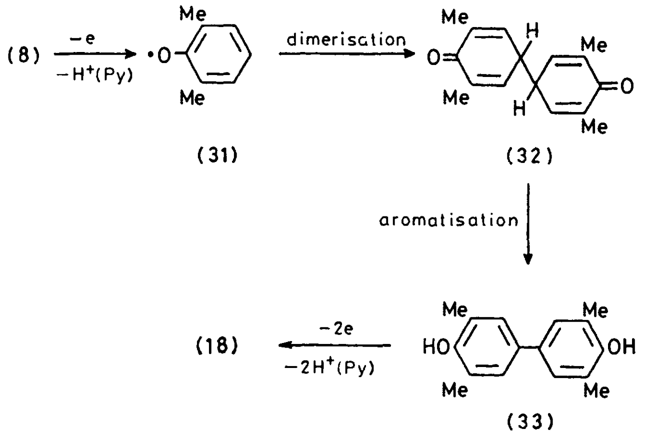
For the other possibility [equation (2)], a very rapid follow-up chemical reaction of (26) other than the proton transfer must be considered because no cathodic peak due to the reduction of (26) was observed under all conditions examined. Though we have no definite experimental proof for the follow-up reaction at hand, again the results obtained by Richards and Evans are suggestive, where very rapid quinol ether formation has been demonstrated in the cyclic voltammetry of phenoxide ions derived from 4-alkyl-2,6-di-t-butylphenols.[8b] Similar formation of a quinol ether (27) from (26) [Scheme 1, step (xii)] will explain the voltammetric results on (2) in the presence of added bases as well as those in the absence of bases. Dimerisation of the cation radical (26) before its deprotonation seems possible because the positive charge can be separated from the reaction centre by rapid intramolecular proton transfer to the imino nitrogen.

The ring-substituted products obtained in the controlled potential electrolysis of the phenolic Schiff's bases (2) in the presence of added bases must result from the reaction of the corresponding phenoxonium ion (22) with the bases. In the presence of added base, the cation radical (26) initially formed at the electrode will undergo both dimerisation to the quinol ether (27) [step (xii) in Scheme 1] and deprotonation by the added base to give the phenoxyl radical (21) [step (x)]. The latter radical will be oxidised further to (22), except for that derived from (2g) (Figure 2 and Table 2). Though the ratio of dimerisation [step (xii)] to deprotonation [step (x)] is not known, the quinol ether (27) thus formed can be converted to (21) according to either of the following processes; continuous shift of the equilibrium between (27) and (26) caused by the deprotonation of (26) to (21) [step (x)], or deprotonation of (27) followed by a similar shift of the equilibrium between the resulting species [(28), (29), and/or (30): also quinol ethers] and the corresponding radicals [(21) and/or (21) + (26)] [step (xv)]. The increase in the peak current of (2) in the presence of pyridine (Figure 3b and Table 1) is ascribed to the further oxidation of the phenoxyl radical (21) formed in this way to the phenoxonium ion (22). The effect of voltage sweep rate on the voltammetric peak of (2d) in the presence of pyridine seems compatible with the steps suggested above. The deprotonation of (26) [step (x)] and/or the reverse step of the dimerisation [step (xii)] may be responsible for the curved plot.

The yields of the ring-substituted products in the controlled potential electrolysis of (2) suggest that the contribution of the corresponding quinone methides [steps (xiii) and (xvi)] to the overall reaction is not significant. The reason why pyridine and other added bases attack the phenoxonium ion (22) derived from (2) at the position *meta* to the original hydroxy-group has been suggested before.[7] Neither evidence against this suggestion nor further support for it was obtained. It is also not clear why substitution did not occur at the other position *meta* to the hydroxy-group, or the position *para* to the imino group.

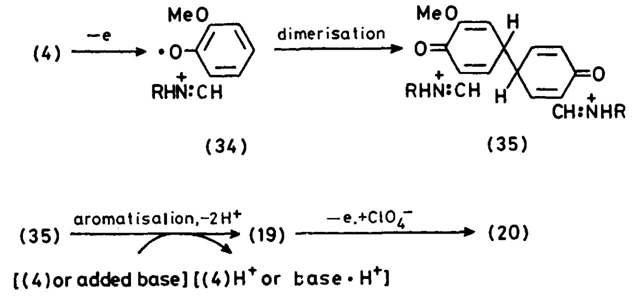
The small cathodic shifts of the voltammetric peak of the phenolic Schiff's base (2) exhibited in the presence of added bases (Table 1) could be attributed either to an increase in the irreversible nature of the process[20] owing to proton transfer between the cation radical (26) and the bases or to the partial contribution of intermolecular hydrogen bonding between (2) and the bases in place of intramolecular hydrogen bonding. The weaker the basicity of the imino nitrogen or the stronger the basicity of added bases, the larger the cathodic shift observed. However, no further evidence to verify these assumptions was obtained.

The side-chain pyridinated phenolic Schiff's base (13g) obtained on electrolysis of (2g) was probably formed from the corresponding quinone methide (25; $R^1 = CH{:}N\text{-}4\text{-}NO_2C_6H_4$, $R^4 = OMe$) * because the phenoxyl radical (21) derived from (2g) will not be oxidised at the potential of the controlled potential electrolysis (0.65 V) as judged from the results in Figure 2d. The low yield of (13g) suggests that some other reactions of the cation radical (26) and/or the corresponding quinol ether (27) take place to afford various unidentified products. These reactions may be responsible for the unexpectedly large voltammetric peak current of (2g) in the presence of added bases (Table 1 and Figure 3c).



SCHEME 2

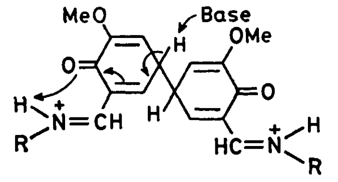
Electrochemical results obtained for phenols without a methyl group *para* to the hydroxy-group can be explained on the basis of similar considerations to those described so far for the electrochemical behaviour of phenols with the methyl group. The process for diphenoquinone (18) formation from 2,6-xylenol (8) in the electrolysis with added pyridine is represented by Scheme 2, which is essentially the same as those suggested in the anodic dimerisation of various phenols.[21] The dimerisation of the corresponding phenoxyl radical (31) should be fast because no cathodic peak due to the reduction of (31) was observed. The effect of the voltage sweep rate on the peak current (Figure 3d) suggests that the aromatisation in Scheme 2 is relatively slow.



SCHEME 3

Similarly Scheme 3 is suggested for formation of the cation radical salts (20) from the phenolic Schiff's bases (4).[1] Dimerisation of the cation radical (34) is expected to be even faster than formation of the quinol ether (27) from the cation radical (26) derived from (2) (Scheme 1) because of the smaller steric hindrance. In the aromatisation of the dimer (35) to the dimeric Schiff's base (19), intramolecular general acid catalysis seems plausible, and this will accelerate the reaction compared with the corresponding process for 2,6-xylenol (8) [Scheme 2, step (32) ⟶ (33)]. Thus the voltammetric peak current of (4) is enhanced in the presence of pyridine (Figure 3a).

It is interesting to compare the effects of pyridine on the electrochemistry of (4d) with those for (4g). Pyridine showed essentially no effect on the peak potential of (4d), while that of (4g) shifted in the cathodic direction by *ca.* 160 mV (Table 1). On controlled potential electrolysis, (4d) gave the cation radical salt (20d) both in the absence (*ca.* 50%) and presence of pyridine (*ca.* 100%). On the other hand, (20g) was not formed on electrolysis in the presence of pyridine (Table 3), though it was formed in the absence of pyridine. As described previously,[1] (20d) is formed on electrolysis of (4d) in methanol but not in methanol containing sodium methoxide. These findings strongly suggest that intermolecular removal of the hydroxy-proton of the cation radical (34) derived from (4) prevents the formation of (20), and that the cation radical (34) dimerises with the proton on the imino nitrogen atom remaining in place.



In conclusion, the principal role of the imino-group *ortho* to the hydroxy-group in the anodic oxidation of the phenolic Schiff's bases (2) and (4) is to catalyse the dimerisation of the corresponding cation radicals (26) and (34) by accepting the proton of the hydroxy-group intramolecularly to remove the positive charge from the reaction centre.

EXPERIMENTAL

Materials.— 2-*Hydroxy*-3-*methoxy*-5-*methylbenzaldehyde* (1) was prepared from 2-methoxy-4-methylphenol (6 g) according to the method for preparing *o*-formylphenols reported by Duff,[22] and was recrystallised from n-hexane to give yellow needles (4 g, 55%), m.p. 50° (Found: C, 64.9; H, 6.0. $C_9H_{10}O_3$ requires C, 65.0; H, 6.1%); $\nu_{max.}$ (Nujol) 1 645 cm^{-1} (C:O), $\lambda_{max.}$ (MeCN) 230 (ε 14 000), 270 (10 000),

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* Various combinations of the steps in Scheme 1 can be considered for quinone methide formation, *e.g.*, (ix)–(x)–(v)–(vii), (ix)–(x)–(vi), (ix)–(xii)–(xiii)–deprotonation, (ix)–(xii)–(xiii)–(xiv) [to give (30)]–(xvi), *etc.*

and 355 (28 000) nm; δ([$^2H_6$]DMSO) 2.27 (3 H, s, Me), 3.87 (3 H, s, OMe), 7.07 (2 H, s, ArH), 10.07 (1 H, s, ArCHO), and 10.24br (1 H, s, OH). *N*-2-Hydroxy-3-methoxy-5-methylbenzylideneamines (2) were prepared by condensation of (1) with appropriate primary amines in absolute ethanol or benzene under reflux for 2—5 h. The crude products were purified by distillation, recrystallisation, or column chromatography on silica gel. Analytical results are summarised in Table 5. *N*-2-Hydroxy-3-methoxybenzylideneamines (4) were obtained from previous work.[1] *N*-(2-Hydroxy-3-methoxybenzyl)-t-butylamine (6) was prepared by sodium borohydride reduction of (4d). $NaBH_4$ (360 mg) was added in portions to a solution of (4d) (1.5 g) in absolute methanol (70 ml) with stirring. Stirring was continued for another 10 min. After the mixture was concentrated to one-tenth of its original volume under reduced pressure, water (50 ml) was added carefully. The resulting mixture was extracted with ether (3 × 20 ml), and the extract was washed and dried. Evaporation of the extract under reduced pressure gave crystals which were recrystallised from n-hexane as leaflets (1.2 g, 82%). *N*-(2-Hydroxy-3-methoxy-5-methylbenzyl)-t-butylamine (5) was prepared similarly from (2d) (1.5 g) and recrystallised as leaflets (1.2 g, 80%). Analytical results are included in Table 5.

TABLE 5

Analytical data for phenols (2), (5), and (6)

		Elemental analysis (%)						
			Found			Required		N.m.r.[a]
Phenol	M.p. (°C)	C	H	N	C	H	N	δ(CH:N)
(2a)	91	67.2	7.4	8.0	67.0	7.3	7.8	8.46
(2b)	42.5	68.4	7.8	7.8	68.4	7.8	7.25	8.49
(2c)	b.p. 98 at 0.02 mmHg	69.15	8.2	6.9	69.5	8.3	6.8	8.49
(2d)	b.p. 120 at 0.02 mmHg	70.15	8.6	6.6	70.6	8.65	6.3	8.44
(2e)	67	74.65	6.3	5.9	74.7	6.3	5.8	8.90
(2f)	70	70.9	6.3	5.2	70.8	6.3	5.2	8.90
(2g)	173	62.75	4.9	9.8	62.9	4.9	9.8	8.92
(5)	90	70.0	9.5	6.3	69.9	9.5	6.3	
(6)	88	68.6	9.1	6.7	68.9	9.15	6.7	

[a] In [$^2H_6$]DMSO, Me_4Si standard.

Phenols (3) and (7), and (8) were recrystallised from methanol–water and n-hexane. Sodium perchlorate was purified as described previously.[23] Pyridinium perchlorate was recrystallised from methanol–ether. Acetonitrile was distilled first from calcium hydride and then from phosphorus pentaoxide after treatment by the method of Mann *et al.*[24] Other chemicals were of reagent grade and were used without further purification.

Apparatus.—Cyclic voltammetry and controlled potential electrolysis (c.p.e.) were carried out essentially as described previously.[25] All voltammetric measurements were carried out at 25 ± 9.1°. From a Yanagimoto V-8 potentiostat and Hokuto Denko HA 104 and HA 101 potentiostat–galvanostats (each different in maximum output), a suitable instrument was selected for use in c.p.e. Constant current electrolysis (c.c.e.) was carried out in an open beaker by using a piece of reticulated glassy carbon (RVC Products Co. RVC 2 × 1-45-s; 8.38 cm^3; area *ca.* 226 cm^2) as the anode and platinum foil as the cathode. The above mentioned potentiostat–galvanostats were used for controlling the current. The anode potential was measured against an aqueous saturated calomel electrode through an agar bridge. The passage of the required electricity was checked with a Hokuto Denko HF-102 coulometer. U.v., i.r., and n.m.r. spectra were obtained using Hitachi 124, EPI-2, and R-20A and R-22 spectrometers, respectively.

The fabrication of glassy carbon electrodes for voltammetry was improved. Thus, a piece of GC-20 glassy carbon rod (Tokai Electrode Manufacturing Co. Ltd.; length 15 mm; diameter 3 mm) was moulded into Diflon tubing (Daikin Kogyo Co. Ltd.; length 30 mm; internal diameter 2.8 mm; external diameter 8 mm) with epoxy resin, after the glassy carbon rod and the tubing were carefully rinsed with acetone: the Diflon tubing swells on heating (150°) and then shrinks to the original size on cooling to room temperature. Diflon was used instead of Teflon because it is harder and its translucency can be used to advantage in finding air bubbles remaining upon moulding the glassy carbon in the tubing. When many bubbles are found, the moulding procedure should be repeated. Electrical contact was made by connecting a brass rod (diameter 2.8 mm) to the glassy carbon with conducting epoxy resin. The surface of the electrode was polished on a Maruto JU-34 vibrating polishing machine with successively finer grades of abrasive, followed by hand polishing with aqueous alumina suspensions (6 μm) to attain a mirror-bright surface. The electrode thus fabricated showed smaller residual currents and better durability against organic solvents than previously used in our laboratory.[26] When the residual current becomes large, the electrode surface is renewed by scraping the edge of the electrode by *ca.* 0.5 mm followed by the polishing procedure.

Analysis and Isolation of Products obtained on Macroscale Electrolysis.—Typical examples of the procedure are described.

(a) *C.p.e. of* (4d) *in acetonitrile.* The phenolic Schiff's base (4d) (83.2 mg) was subjected to electrolysis in acetonitrile (50 ml) containing 0.1M-$NaClO_4$ at 0.65 V at room temperature until the value of current became <5% of the initial value. From the current–time curve 31.5 C, which corresponded to *n* 0.85, was found to be consumed. The solution from electrolysis showed a cyclic voltammogram which coincided with that of (4d) in the presence of excess of perchloric acid, and on addition of excess of pyridine the solution showed a cyclic voltammogram which coincided with that of (4d) under the same conditions. The absorption spectra of the solution from electrolysis coincided with those of (4d) in the presence of perchloric acid. Thus (4d) was partly protonated on electrolysis. The amount of the protonated form was determined by measuring the peak height of the voltammograms described above, and by measuring the absorbance of the solution from electrolysis. The two measurements agreed well. In this case 45% of (4d) was recovered.

(b) *C.p.e. of* (4d) *in acetonitrile containing an excess of pyridine.* The Schiff's base (4d) (94.2 mg) was subjected to electrolysis in acetonitrile (100 ml) containing pyridine (1 ml) and 0.1M-$NaClO_4$ at 0.6 V until the value of the current became <1% of the initial value. The anolyte was evaporated to dryness under reduced pressure and the residue was washed successively with small amounts of ether, chloroform, and water (three times with each solvent). Recrystallisation of the residue from methanol gave yellow needles (127 mg 75%), which were identified as N-(2-N-*t-butyliminomethyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)-*pyridinium perchlorate* (9d), m.p. 230° (decomp.) (Found: C, 54.7; H, 5.8; N, 7.1. $C_{18}H_{23}ClN_2O_6$ requires C, 54.2; H, 5.8; N, 7.0%); $\nu_{max.}$ (Nujol) 3 147, 1 637, and 1 092 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.19 (9 H, s, CMe_3), 1.86 (3 H, s, ArMe), 3.87 (3 H, s, ArOMe), 7.00 (1 H, s, ArH), 7.58 (1 H, s, ArCH:N), 8.31—9.10 (5 H, m, Py^+H), and 14.79br (1 H, s, ArOH).

Other pyridinated products were obtained similarly. Their analytical and physical data are as follows.

N-(2-N-*Isopropyliminomethyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)*pyridinium perchlorate* (9c) had m.p. 235° (decomp.) (Found: C, 53.3; H, 5.6; N, 7.2. $C_{17}H_{21}ClN_2O_6$ requires C, 53.1; H, 5.5; N, 7.3%); $\nu_{max.}$ (Nujol) 3 164, 1 641, and 1 100 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.17 (6 H, d, *J* 6.5 Hz, CH*Me*$_2$), 1.87 (3 H, s, ArMe), 3.46 (1 H, septet, *J* 6.5 Hz, C*H*Me$_2$), 3.86 (3 H, s, ArOMe), 7.04 (1 H, s, ArH), 7.85 (1 H, s, ArC*H*:N), 8.32—9.16 (5 H, m, Py^+H), and 14.50br (1 H, s, ArOH). N-(2-N-*Phenyliminomethyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)*pyridinium perchlorate* (9e) had m.p. 210° (decomp.) (Found: C, 57.3; H, 4.6; N, 6.8. $C_{20}H_{19}ClN_2O_6$ requires C, 57.35; H, 4.6; N, 6.7%); $\nu_{max.}$ (Nujol) 3 155, 1 627, and 1 100 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.98 (3 H, s, ArMe), 3.98 (3 H, s, ArOMe), 7.10 (1 H, s, ArH), 7.20 (5 H, m, Ar'H), 8.41 (1 H, s, ArC*H*:N), 8.35—9.25 (5 H, m, Py^+H), and 13.03br (1 H, s, ArOH). N-(2-N-p-*Methoxyphenyliminomethyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)*pyridinium perchlorate* (9f) had m.p. 273° (decomp.) (Found: C, 56.1; H, 4.8; N, 6.4. $C_{21}H_{21}ClN_2O_7$ requires C, 56.2; H, 4.7; N, 6.2%); $\nu_{max.}$ (Nujol) 3 190, 1 632, and 1 090 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.95 (3 H, s, ArMe), 3.77 and 3.97 (6 H, 2 × s, ArOMe and Ar'OMe), 6.93 and 7.12 (4 H, 2 × d, *J* 9 Hz, Ar'H), 7.28 (1 H, s, ArH), 8.30 (1 H, s, ArC*H* : N), 8.36—9.23 (5 H, m, Py^+H), and 13.30br (1 H, s, ArOH). N-(3-*Formyl*-4-*hydroxy*-5-*methoxybenzyl*)*pyridinium perchlorate* (12) had m.p. 158° (Found: C, 48.7; H, 4.1; N, 4.05. $C_{14}H_{14}ClNO_7$ requires C, 48.9; H, 4.1; N, 4.1%); $\nu_{max.}$ (Nujol) 3 630, 3 150, and 1 085 cm^{-1}; $\delta([^2H_6]DMSO)$ 3.91 (3 H, s, ArOMe), 5.80 (2 H, s, $ArCH_2Py^+$), 7.51 (2 H, s, ArH), 8.15—9.21 (5 H, m, Py^+H), 10.32 (1 H, s, ArCHO), and 10.51br (1 H, s, ArOH).

N-(3-N-p-*Nitrophenyliminomethyl*-4-*hydroxy*-5-*methoxybenzyl*)*pyridinium perchlorate* (13g) had m.p. 180—182° (Found: C, 51.2; H, 4.1; N, 9.5. $C_{20}H_{18}ClN_3O_8$ requires C, 51.8; H, 3.9; N, 9.1%); $\nu_{max.}$ (Nujol) 3 110, 1 625, and 1 095 cm^{-1}; $\delta([^2H_6]DMSO)$ 2.08 (3 H, s, Me), 3.91 (3 H, s, ArOMe), 5.79 (2 H, s, $ArCH_2Py^+$), 6.62 and 7.94 (4 H, s × d, *J* 9 Hz, Ar'H), 7.51 (2 H, s, ArH), 8.18—9.21 (6 H, m, Py^+H and ArC*H*:N), and 12.50 (1 H, s, ArOH). This pyridinium salt (53.4 mg) was hydrolysed in 10% aqueous HCl (70 ml) on a water-bath for 10 h. From the solution, the corresponding aldehyde (12) (31.2 mg) crystallised on standing for one day. N-(3,5-*Di-t-butyl*-4-*hydroxybenzyl*)*pyridinium perchlorate* (15) had m.p. 231° (decomp.) (Found: C, 60.3; H, 7.2; N, 3.5. $C_{20}H_{28}ClNO_5$ requires C, 60.4; H, 7.1; N, 3.5%); $\nu_{max.}$ (Nujol) 3 640, 1 642, and 1 090 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.37 (18 H, s, CMe_3), 5.67 (2 H, s, ArC*H*$_2$Py$^+$), 7.15 (1 H, s, ArOH), 7.25 (2 H, s, ArH), and 8.10—9.15 (5 H, m, Py^+H).

The ring-pyridinated Schiff's base (9d) (84.3 mg) was hydrolysed in 10% aqueous HCl (70 ml) on a water-bath for 10 h. When the solution was allowed to stand for one day, needles were deposited (60 mg, 83%), which were recrystallised from methanol–water and identified as N-(2-*formyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)*pyridinium perchlorate* (14), m.p. 233° (decomp.) (Found: C, 49.0; H, 4.1; N, 4.2. $C_{14}H_{14}ClNO_7$ requires C, 48.9; H, 4.1; N, 4.1%); $\nu_{max.}$ (Nujol) 3 206, 1 681, and 1 100 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.96 (3 H, s, ArMe), 4.02 (3 H, s, ArOMe), 7.44 (1 H, s, ArH), 8.33—9.14 (5 H, m, Py^+H), 10.28 (1 H, s, ArCHO), and 10.83br (1 H, s, ArOH).

(c) *C.p.e. of* (4d) *in acetonitrile containing an excess of imidazole.* The Schiff's base (4d) (127.9 mg) was subjected to electrolysis in acetonitrile (50 ml) containing imidazole (200 mg) and 0.1M-$NaClO_4$ at 0.55 V as described in (b). The anolyte was concentrated to one-tenth of its original volume under reduced pressure, and then diluted with water (50 ml). The resulting mixture was extracted with chloroform (2 × 50 ml), and the extract was washed and dried. The chloroform was removed under reduced pressure and the residue was subjected to column chromatography on neutral alumina with chloroform–methanol (7 : 1) as eluant. The yellow crystals obtained (83.0 mg) from the first effluent were recrystallised from n-hexane to give yellow needles, which were identified as N-(2-N-t-*butyliminomethyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)*imidazole* (10d), m.p. 156° (Found: C, 66.8, H, 7.4; N, 14.5. $C_{16}H_{21}N_3O_2$ requires C, 66.9; H, 7.4; N, 14.6%); $\nu_{max.}$ (Nujol) 3 165 and 1 628 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.16 (9 H, s, CMe_3), 1.88 (3 H, s, ArMe), 3.83 (3 H, s, ArOMe), 6.94 (1 H, s, ArH), 7.41 (1 H, s, ArC*H*:N), 7.12, 7.27, and 7.72 (3 H, 3 × m, imidazole), and 14.50br (1 H, s, ArOH); *m/e* 287 (M^+). A little of the anolyte was used to estimate the yield of (10d) by liquid chromatography, which was carried out by using a Waters 6000-A solvent delivery system with a U6K universal injector and a JASCO UVIDEC-1 spectrophotometer [Bondapak C_{18}–Corasil (37—50 μm); 1/8 in × 2 ft column; 70% (v/v) aqueous methanol; 3 ml min^{-1}; 420 nm]. The yield was found to be 71%.

The following anodic substitution products were obtained similarly. N-(2-N-*Isopropyliminomethyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)*imidazole* (10c) had m.p. 118° (Found: C, 65.6; H, 7.0; N, 15.3. $C_{15}H_{19}N_3O_2$ requires C, 65.9; H, 7.0; N, 15.4%); $\nu_{max.}$ (Nujol) 3 190 and 1 622 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.19 (6 H, d, *J* 6.5 Hz, CH*Me*$_2$), 1.90 (3 H, s, ArMe), 3.42 (1 H, septet, *J* 6.5 Hz, C*H*Me$_2$), 3.84 (3 H, s, ArOMe), 7.02 (1 H, s, ArH), 7.14, 7.29, and 7.72 (3 H, 3 × m, imidazole), 7.58 (1 H, s, ArC*H*:N), and 14.60br (1 H, s, ArOH); *m/e* 273 (M^+). N-(2-N-t-*Butyliminomethyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)*benzimidazole* (11d) had m.p. 165° (Found: C, 71.0; H, 6.8; N, 12.4. $C_{20}H_{23}N_3O_2$ requires C, 71.2; H, 6.9; N, 12.45%); $\nu_{max.}$ (Nujol) 3 139 and 1 629 cm^{-1}; $\delta([^2H_6]DMSO)$ 1.03 (9 H, s, CMe_3), 1.93 (3 H, s, ArMe), 3.87 (3 H, s, ArOMe), 7.06 (1 H, s, ArH), 7.34 (1 H, s, Ar-C*H* : N), [7.02 (1 H, m), 7.25 (1 H, m), 7.78 (1 H, m), and 8.35 (1 H, s), (benzimidazole)], and 14.50br (1 H, s, ArOH); *m/e* 337 (M^+). N-(2-N-*Isopropyliminomethyl*-3-*hydroxy*-4-*methoxy*-6-*methylphenyl*)*benzimidazole* (11c) had m.p. 157° (Found: C, 70.3; H, 6.55; N, 12.7. $C_{19}H_{21}N_3O_2$ requires C, 70.6; H, 6.55; N, 13.0%); $\nu_{max.}$ (Nujol) 3 145 and 1 633 cm^{-1}; δ([$^2H_6$]DMSO) [1.04 (3 H, d, *J* 6.5 Hz) and 1.10 (3 H, d, *J* 6.5 Hz) (CH*Me*$_2$)], 1.77 (3 H, s, ArMe), 3.28 (1 H, septet, *J* 6.5 Hz, C*H*Me$_2$), 3.86 (3 H, s, ArOMe), 7.08 (1 H, s, ArH), 7.54 (1 H, s, ArC*H* : N), [7.00 (1 H, m), 7.25 (2 H, m), 7.78 (1 H, m), and 8.32 (1 H, s) (benzimidazole)], and 14.67br (1 H, s, ArOH); *m/e* 323 (M^+).

(d) *C.p.e. of* 2,6-*xylenol* (8) *in acetonitrile containing an excess of pyridine*. The phenol (8) (241.9 mg) was subjected to electrolysis in acetonitrile (50 ml) containing pyridine (0.5 ml) and 0.1M-$NaClO_4$ at 0.7 V until the value of the current became $<1\%$ of the initial value. The anolyte was evaporated to dryness under reduced pressure, and water (50 ml) was added to the residue. The resulting mixture was extracted with chloroform (2 × 50 ml), and the extract was washed and dried. The chloroform was removed under reduced pressure and the residue was recrystallised from acetic acid to give deep red needles (274.9 mg, 79%), which were identified as 3,3′,5,5′-tetramethyldiphenoquinone (18), m.p. 213° (decomp.) (lit.,[27] 210—215°). The i.r. and the u.v. spectra of (18) coincided with those reported.[4] Formation of (18) has been demonstrated on electrolysis of (8) in acetonitrile containing 2,6-lutidine.[4]

(e) *C.c.e. of* (1) *in acetonitrile containing an excess of pyridine*. The hydroxybenzaldehyde (1) (199.2 mg) was subjected to electrolysis in acetonitrile (50 ml) containing pyridine (0.5 ml) and 0.2M-pyridinium perchlorate at 200 mA (current density *ca.* 0.88 mA cm^{-2}). 229.9 Coulombs, which were required for a two-electron oxidation, were allowed to pass. The solution from electrolysis was evaporated to dryness under reduced pressure. After being washed with ether (3 × 20 ml), the residue was recrystallised from methanol–water to give (12) (289.7 mg). From the washings (1) (11.3 mg) was recovered.

(f) *C.c.e. of* (7) *in acetonitrile containing methanol*. The phenol (7) (214.7 mg) was subjected to electrolysis in acetonitrile (50 ml) containing methanol (1 ml) and 0.1M-Et_4NClO_4 at 200 mA. A mixture (198.4 mg) of (16) and (17), obtained by essentially the same work-up as reported by Ronlăn and Parker,[10] was analysed by n.m.r. ($CDCl_3$) to estimate the product ratio.

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