# Anodic Oxidation of Schiff's Bases. Part II.[1] Anodic Pyridination of *N*-Benzylidene-*p*-anisidines in Acetonitrile

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Anodic oxidation of *N*-benzylidene-*p*-anisidines in acetonitrile containing excess of pyridine results in the formation of a pyridinated Schiff's base in which the pyridinium group is *ortho* to the azomethine nitrogen atom on the anisidine ring. The pyridination process was investigated by cyclic voltammetry and controlled potential electrolysis at a glassy-carbon electrode. It is suggested that the sequence of pyridination is one-electron transfer from the lone pair of the azomethine nitrogen atom, proton transfer to pyridine from the *ortho*-position of the anisidine ring to the azomethine linkage, a further one-electron transfer to form a carbonium ion, and attack of pyridine. When pyridine was present in an equimolar amount or in slight excess, the behaviour at the electrode was rather complex: probably anodic acetamidation and/or anodic hydroxylation occurred.

PREVIOUSLY we reported on the oxidation of *N*-benzylidene-*p*-anisidines at a glassy-carbon electrode in acetonitrile with and without added water.[1] A different reaction occurred at the electrode in the presence of pyridine: on controlled potential electrolysis pyridinated Schiff's bases (I) were formed.

Several possible mechanisms for anodic pyridination of aromatic hydrocarbons have been suggested.[2,3] One of these involves an initial one-electron transfer, followed by nucleophilic addition of pyridine and a further one-electron transfer.[3] Loss of the proton has been stated to follow the second electron transfer. Similarly in the anodic acetoxylation of aromatic hydrocarbons, proton transfer (deprotonation of the substrate) has been suggested to occur after the transfer of two electrons, though the stage at which nucleophilic attack of the acetoxy-group occurs differs in nuclear and side-chain acetoxyl-

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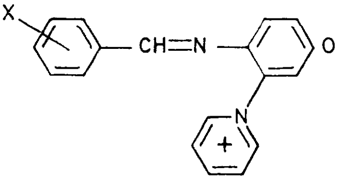
[1] Part I, M. Masui and H. Ohmori, *J.C.S. Perkin II*, 1972, 1882.

[2] H. Lund, *Acta Chem. Scand.*, 1957, **11**, 1323; V. D. Parker and L. Eberson, *Chem. Comm.*, 1969, 451; L. Marcoux, *J. Amer. Chem. Soc.*, 1971, **93**, 538.

[3] G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, 1969, **91**, 4584; V. D. Parker and L. Eberson, *Tetrahedron Letters*, 1969, 2843; V. D. Parker, *J. Electroanalyt. Chem.*, 1972, **36**, 8.

ations.[4,5] On the other hand, the sequence of acetoxylation of amides has been reported to be one-electron



(I)

transfer from the lone pair of the amide nitrogen atom, proton transfer from one of the alkyl groups attached to the nitrogen to form a carbon radical, a further one-electron transfer to form a carbonium ion, and attack of an acetate ion.[6] It was of interest to investigate the details of anodic pyridination of Schiff's bases in the light of these mechanisms, and to compare the mechanism with those suggested for pyridination of aromatic hydrocarbons. The initial electron transfer in the oxidation of *N*-benzylidene-*p*-anisidines is from the lone pair of the azomethine nitrogen atom.[1]

This paper reports the results of cyclic voltammetry and controlled potential electrolysis of *N*-benzylidene-*p*-anisidines in acetonitrile containing pyridine.

## RESULTS

*Cyclic Voltammetry of* N-*Benzylidene*-p-*anisidines*.—*N*-Benzylidene-*p*-anisidines showed two anodic peaks in acetonitrile containing 1% pyridine (*ca.* 0·124M) and 0·1M-sodium perchlorate. The peak current of the first wave was nearly twice as large as that observed in the absence of pyridine. A typical example is shown in Figure 1. The values of the peak currents and the peak potentials are summarized in Table 1. A plot of the $i_p$ value of the first wave against the square root of the scan rate at scan rates of 11—192 mV s$^{-1}$ displayed downward curvature, indicating that some electrochemical process occurred at the first wave.[7] As described previously,[1] a linear relationship was obtained in the absence of pyridine for the same range of scan rates.

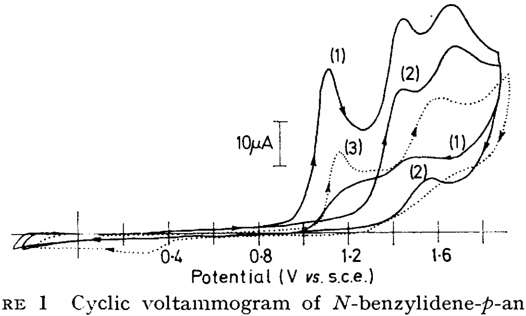


FIGURE 1 Cyclic voltammogram of *N*-benzylidene-*p*-anisidine (1 mM) in acetonitrile with 0·1M-NaClO$_4$ at a scan rate of 47 mV s$^{-1}$: (1), containing 1% pyridine (the peak near 1·65 V is due to the oxidation of pyridine; (2), containing 1% pyridine after electrolysis for 130 min at 1·10 V; (3), in the absence of pyridine (from ref. 1)

The effects of various pyridines on the first wave of several *N*-benzylidene-*p*-anisidines are summarized in Table 2. The value of the peak current of the first wave approached a constant value even at low concentrations of pyridines. Hindered substrates, such as 2-picoline and 2,6-lutidine, were as effective as the unhindered compounds, pyridine and 3,5-lutidine. On the other hand, the shape of the current potential curves, other than the first wave, was changed by the kind and concentration of the pyridines. Some examples are illustrated in Figure 2. At low concentrations of pyridines (<1·5 mM), two peaks were observed near 1·50 and 1·71 V in addition to the first wave (Figure 2, peaks A and B; in the case of 2,6-lutidine peak A was observed near 1·57 V). In the case of pyridine, 3,5-lutidine, and 2-picoline, a new peak (peak C in Figure 2) appeared near 1·45 V with an increase in the concentration of pyridines, and this was accompanied by decrease and/or disappearance of peaks A and B. Pyridine and 3,5-lutidine were almost equally effective in causing the appearance and increase of the new peak C. 2-Picoline was less

TABLE 1

Results of cyclic voltammetry of substituted *N*-benzylidene-*p*-anisidines in acetonitrile containing 1% pyridine and 0·1M-NaClO$_4$. Voltage scan rate, 47 mV s$^{-1}$. Concentration of Schiff's base, 1 mM. Geometric electrode area, 0·071 cm$^2$

| Compound | First wave $E_{p_1}$/V *vs.* s.c.e. | $i_p$/μA | Second wave $E_{p_2}$/V *vs.* s.c.e. |
|---|---|---|---|
| $XC_6H_4CH{=}NC_6H_4OMe$(*p*) | | | |
| X = H | 1·12 | 35·9 | 1·45 |
| *p*-OMe | 1·05 | 35·0 | 1·33 |
| *p*-Me | 1·09 | 35·8 | 1·42 |
| *p*-Cl | 1·14 | 35·0 | 1·47 |
| *m*-Cl | 1·15 | 36·6 | 1·50 |
| *o*-Cl | 1·15 | 35·7 | 1·50 |
| *p*-$NO_2$ | 1·19 | 35·7 | 1·55 |
| $Ph_2C{=}NC_6H_4OMe$(*p*) | 1·04 | 29·9 | 1·37 |

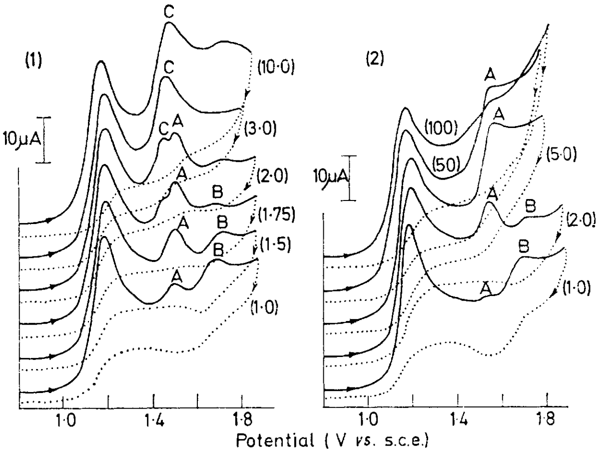


FIGURE 2 Cyclic voltammograms of *N*-*p*-chlorobenzylidene-*p*-anisidine (1 mM) in acetonitrile in the presence of various concentrations of (1) pyridine and (2) 2,6-lutidine with 0·1M-NaClO$_4$ at a scan rate of 47 mV s$^{-1}$ [values in parentheses show concentrations (mM) of pyridine added]

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[4] M. Leung, J. Herz, and H. Salzberg, *J. Org. Chem.*, 1965, **30**, 310; L. Eberson and K. Nyberg, *J. Amer. Chem. Soc.*, 1966, **88**, 1686.

[5] L. Eberson and K. Nyberg, *Acta Chem. Scand.*, 1964, **18**, 1568; L. Eberson, *J. Amer. Chem. Soc.*, 1967, **89**, 4669; F. Mango and W. Bonner, *J. Org. Chem.*, 1964, **29**, 1367.

[6] S. D. Ross, M. Finkelstein, and R. C. Peterson, *J. Amer. Chem. Soc.*, 1964, **86**, 2745; *J. Org. Chem.*, 1966, **31**, 128.

[7] R. N. Adams, 'Electrochemistry at Solid Electrodes,' Dekker, New York, 1969, chs. 5 and 8.

effective, and a higher concentration was required for development of peak C. Addition of 2,6-lutidine did not result in the distinct appearance of the corresponding peak C, though high concentrations resulted in a reduction of the size of peak A near 1·57 V (Figure 2).

When 2 mM-acetamide was added to a solution of *N*-*p*-chlorobenzylidene-*p*-anisidine (1 mM) in acetonitrile containing 2 mM-pyridine or -3,5-lutidine, peak A increased, peak C decreased, and peak B disappeared (*cf.* Figure 2). When 1M-water was added to a solution of the *N*-*p*-chloro-compound (1 mM) in acetonitrile containing any one of the pyridines at a concentration of 1 mM, the first wave increased *ca.* 1·15 fold and peaks A and B disappeared (*cf.* Table 2).

*Controlled Potential Electrolysis.*—Table 3 summarizes the results on controlled potential electrolysis. Details of the procedures and identification of the products are described in the Experimental section.

A cyclic voltammogram of the solution after electrolysis showed a peak corresponding to the second peak observed

TABLE 2

Effect of pyridines on the first wave of *N*-benzylidene-*p*-anisidines in acetonitrile containing 0·1M-$NaClO_4$. Concentration of Schiff's base, 1 mM

| Compound | Concentration of pyridines (mM) | Pyridine | | 2-Picoline | | 3,5-Lutidine | | 2,6-Lutidine | |
|---|---|---|---|---|---|---|---|---|---|
| | | Ratio [a] | $E_{p_1}$ [b] | Ratio [a] | $E_{p_1}$ [b] | Ratio [a] | $E_{p_1}$ [b] | Ratio [a] | $E_{p_1}$ [b] |
| *N*-Benzylidene-*p*-anisidine | None | (1·00) [c] | (1·16) [c] | | | | | | |
| | 0·5 | 1·41 | 1·15 | | | | | | |
| | 1·0 | 1·85 | 1·17 | 1·99 | 1·16 | | | 1·89 | 1·18 |
| | 1·5 | 1·99 | 1·17 | | | | | | |
| | 2·0 | 1·97 | 1·17 | 2·11 | 1·18 | | | 2·03 | 1·18 |
| | 5·0 | 2·02 | 1·17 | 2·07 | 1·17 | | | 1·97 | 1·17 |
| | 10 | 2·03 | 1·15 | 2·05 | 1·16 | | | 1·94 | 1·16 |
| | 50 | | | 1·98 | 1·15 | | | 2·04 | 1·16 |
| | 75 | | | | | | | 2·03 | 1·16 |
| | 85 | | | | | | | 1·94 | 1·16 |
| | 100 | 2·06 | 1·13 | 1·98 | 1·14 | | | 1·78 | 1·15 |
| *N*-*p*-Chlorobenzylidene-*p*-anisidine | None | (1·00) [c] | (1·18) [c] | | | | | | |
| | 1·0 | 1·72 | 1·19 | | | 1·58 | 1·19 | 1·81 | 1·19 |
| | 1·5 | 1·74 | 1·20 | | | | | | |
| | 1·75 | 1·76 | 1·19 | | | | | | |
| | 2·0 | 1·77 | 1·19 | | | 1·73 | 1·19 | 1·85 | 1·20 |
| | 3·0 | 1·78 | 1·19 | | | | | | |
| | 5·0 | 1·79 | 1·18 | | | 1·78 | 1·17 | 1·80 | 1·20 |
| | 10 | 1·78 | 1·17 | | | 1·80 | 1·16 | 1·75 | 1·20 |
| | 50 | 1·85 | 1·14 | | | 1·95 | 1·15 | 1·75 | 1·18 |
| | 100 | 1·87 | 1·12 | | | 2·05 | 1·13 | 1·63 | 1·18 |
| *N*-Diphenylmethylene-*p*-anisidine | None | (1·00) [c] | (1·04) [c] | | | | | | |
| | 1·0 | 1·57 | 1·06 | | | | | 1·62 | 1·05 |
| | 2·0 | 1·57 | 1·06 | | | | | 1·69 | 1·06 |
| | 5·0 | 1·54 | 1·06 | | | | | 1·79 | 1·06 |
| | 10 | 1·56 | 1·05 | | | | | 1·91 | 1·06 |
| | 50 | 1·62 | 1·06 | | | | | 2·07 | 1·06 |
| | 100 | 1·67 | 1·06 | | | | | 2·06 | 1·07 |

[a] Ratio of the value of the peak current in the presence of the indicated amount of pyridines to that in the absence of pyridines. [b] V *vs.* s.c.e. [c] The value in the absence of pyridines is cited for comparison.

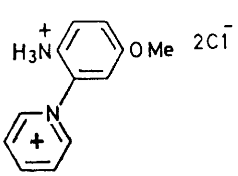
TABLE 3

Results of controlled potential electrolysis in acetonitrile containing 1% pyridine [a]

| Compound | Applied potential (V *vs.* s.c.e.) | *n* Value [b] | Products identified | Amount of sample (mg) |
|---|---|---|---|---|
| *N*-Benzylidene-*p*-anisidine | 1·10 [c] | 2·07 | (I; X = H) | 48·1 |
| | 1·10 | 2·07 | (I; X = H) | 41·7 |
| | 1·10 | 2·22 | (I; X = H) [d] | 116·7 |
| | 1·10 | 2·03 | (I; X = H) | 403·6 |
| *N*-*p*-Methoxybenzylidene-*p*-anisidine | 1·05 | 2·16 | (I; X = *p*-OMe) | 471·2 |
| *N*-*p*-Chlorobenzylidene-*p*-anisidine | 1·15 | 2·29 | (I; X = *p*-Cl) [d] | 442·0 |
| | 1·15 | 2·21 | (I; X = *p*-Cl) [e] | 459·6 |
| | 1·15 [c] | 1·82 | (I; X = *p*-Cl) | 512·5 |
| *N*-Diphenylmethylene-*p*-anisidine | 1·05 | 1·90 | *f* | 30·6 |
| | 1·05 | 1·97 | (II) [f,g] | 152·1 |

[a] The volume of anolyte was 100 ml in all cases. 0·1M-$NaClO_4$ was used as supporting electrolyte. [b] *n* Values were calculated from the quantity of electricity consumed during electrolysis, this being obtained from the area below the current–time curve (see Experimental section). [c] Electrolysis was carried out at low temperature (<5 °C). [d] A small amount of the free base form of (II) was obtained as the perchlorate [compound (VIII), see Experimental section]. [e] [$^2H_5$]Pyridine was used instead of normal pyridine, and hence the pyridinated Schiff's base contained the [$^2H_5$]pyridinium group. [f] A cyclic voltammogram of the solution from electrolysis suggested the formation of a pyridinated Schiff's base (see text). [g] 4-Methoxy-2-pyridiniumanilinium dichloride was isolated (see text and Experimental section).

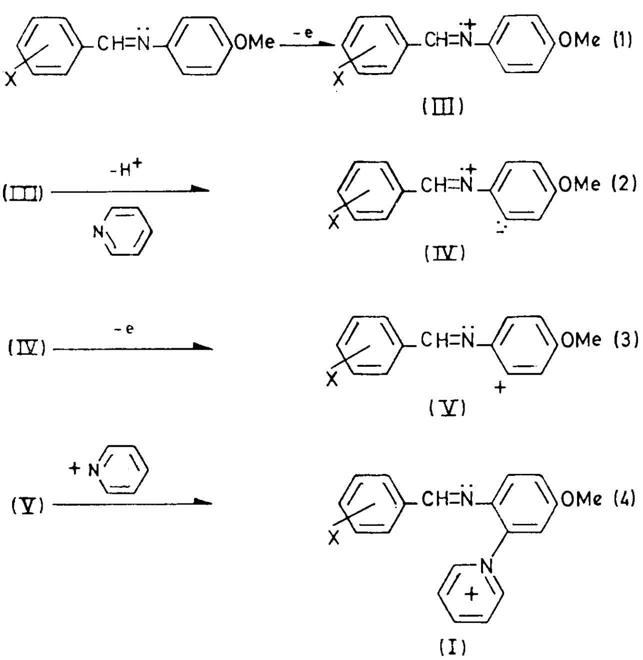
in cyclic voltammetry of the starting Schiff's base in acetonitrile containing 1% pyridine (Figure 1). The same cyclic voltammogram was obtained when the pyridinated Schiff's bases (I) were subjected to cyclic voltammetry under the same conditions. In the case of *N*-diphenylmethylene-*p*-anisidine, an attempt to isolate the pyridinated Schiff's base was unsuccessful presumably because it is easily hydrolysed. However, the voltammogram of a solution of *N*-diphenylmethylene-*p*-anisidine after electrolysis was similar to that described above, and 4-methoxy-2-pyridiniumanilinium dichloride (II) was isolated from the solution (Table 3).* Since the solvent used for isolation of the products (see Experimental section) was contaminated with water, the pyridinated Schiff's base was hydrolysed during the prolonged contact with the solvents involved in the method. These facts strongly suggest that the reaction of this compound at the electrode is the same as that of other Schiff's bases.



(II)

DISCUSSION

From the results the process of anodic pyridination of *N*-benzylidene-*p*-anisidines in the presence of sufficient pyridine may be described by the Scheme where reaction (1) is the same as that suggested to occur in the absence of pyridine.[1] The observations of the controlled potential electrolyses (see Experimental section) suggest that the oxidation of pyridine itself did not participate in the reactions under the experimental conditions.



SCHEME

The fact that hindered pyridines, such as 2-picoline and 2,6-lutidine, were as effective as unhindered ones in increasing the first wave (Table 2) strongly suggests that the primary role of the pyridines is to act as a base, or as a proton acceptor. It has been reported that in the anodic pyridination of anthracene derivatives, 2,6-lutidine was *ca.* 30-fold less reactive toward a cation radical than 3,5-lutidine when acting as a carbon-attacking nucleophile, but as proton-seeking bases both lutidines reacted nearly stoicheiometrically.[8] Even in the presence of a high concentration of 2,6-lutidine the peak near 1·45 V (peak C) was not distinct (Figure 2). This peak is attributable to further oxidation of the pyridinated Schiff's base (I) as suggested from the results of cyclic voltammetry (Figure 1). In reaction (2) the fact that the proton transfer occurs at the aniline ring and not at the azomethine carbon atom is supported by the observation that *N*-diphenylmethylene-*p*-anisidine showed essentially the same behaviour at the electrode as the other Schiff's bases. The nitrogen lone pair of *N*-benzylideneanilines has been shown to conjugate with the aniline part of the molecule.[9] The positive charge generated in (III) will tend to be localized on the aniline ring, and hence deprotonation occurs at the ring. Pyridination, and hence proton transfer, did not occur at the methoxy-group since the methoxy-protons remained unchanged judging from the n.m.r. spectra of the pyridinated Schiff's bases produced (see Table 4).

Upon controlled electrolysis at the potential of the first wave two electrons per molecule of *N*-benzylidene-*p*-anisidine were consumed (Table 3). Thus reactions (1)—(3) can be attributed to the first wave though it cannot be decided from the present results alone whether reactions (1)—(3) occur stepwise or together, as suggested in the anodic acetoxylation of aromatic hydrocarbons.[5] A plot of the peak potentials of the first wave in the presence of 1% pyridine against those in the absence of pyridine gave a straight line with a slope of nearly unity (*cf.* Table 1). The latter potentials were linearly related to the $\sigma^+$ values of the substituents in the benzylidene ring.[1] These findings suggest that reaction (1) is rate-determining in the present case also. As seen from Table 2, at higher concentrations of pyridines the peak potential of the first wave shifted slightly towards a less positive potential though the peak current remained nearly constant. This could be related to the involvement of a concerted mechanism rather than a stepwise one.

Since the acetonitrile used in this study contained a small amount of water (0·025%) as described previously,[1]

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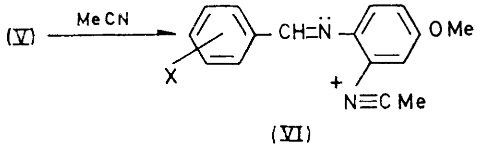
* 4-Methoxy-2-pyridiniumanilinium dichloride was oxidized at 0·89 V in acetonitrile containing 1% pyridine, which is less positive than the potential used in controlled potential electrolysis of the Schiff's bases. Hence if the compound was produced during the electrolysis, it should be oxidized further at the potential applied.

[8] V. D. Parker and L. Eberson, *Tetrahedron Letters*, 1969, 2839.

[9] K. Tabei and E. Saitou, *Bull. Chem. Soc. Japan*, 1969, **42**, 1440; M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, 1971, **93**, 586 and 590; J. W. Pavlik and A. van Putten, *Tetrahedron*, 1971, **27**, 3007, 3301.

the possibility of water playing a similar role as in the absence of pyridine [1] should also be considered. Water may attack the intermediate cation radical (III) which is hydrolysed to the anisidine cation radical and the corresponding benzaldehyde. However, 0·025% water is not sufficient to compete with the excess of pyridine for the intermediate cation radical (III). The involvement of water would be observed if the rate of the reaction with the intermediate (III) ($v_{H_2O}$) is comparable with that of the reaction of pyridine with the intermediate ($v_{Py}$). As shown in the cyclic voltammetry of Schiff's bases in the presence of added water,[1] at least 1% water was required for the second wave to merge with the first (*cf.* dashed curve in Figure 1) even in the case of the most reactive Schiff's base, *N*-*p*-nitrobenzylidene-*p*-anisidine. On the other hand, 1 mM-pyridine almost doubled the $i_p$ value of the first wave (Table 2). These findings strongly suggest that $v_{H_2O}$ is not comparable with $v_{Py}$ under the present conditions.

The peak observed near 1·71 V (peak B in Figure 2) at lower concentrations of added pyridines must be due to further oxidation of the ion (V). The peak disappeared when the concentration of pyridines was increased, or when 1M-water was added. In the latter case, the first wave increased as expected. If the ion (V) is attacked by water and a hydroxylated compound is formed, it will be oxidized more easily than the original Schiff's base and hence will be oxidized at the potential of the first wave. The positive charge on the ion (V) lies closer to the nitrogen lone pair than that on (I), and it may be conjugated with the lone pair. Thus the ion (V) is expected to be oxidized at a more positive potential than (I), in agreement with the observed results.



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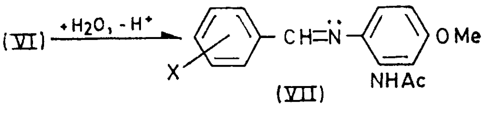

(6)

The nature of the peak near 1·50 V (peak A in Figure 2) is uncertain. However, it is possible that anodic acetamidation occurs as reported by Eberson and Nyberg for the oxidation of pivalic acid [10] and polymethylbenzenes [11] in acetonitrile. At lower concentrations of pyridines, the peak increased with concentration though it disappeared at higher concentrations (Figure 2). The peak also disappeared when 1M-water was added, but increased when acetamide (2 mM) was added to the solution. These observations suggest the reactions (3) and (6), by analogy with the reported acetamidation.[10,11] The acetonitrile used was contaminated with a little water which may participate in reaction (6). In the acetamidation [10,11] the small quantity of water in the acetonitrile has been suggested to play a similar role. In the presence of sufficient water (1M) reaction (5) is replaced by hydroxylation and the peak near 1·50 V disappears. At higher concentrations of pyridines, reaction (4) will take place in preference to reaction (5). Thus the peak near 1·50 V (peak A in Figure 2) can be ascribed to further oxidation of (VII). Further evidence is required to establish the occurrence of reactions (5) and (6).

## EXPERIMENTAL

*Materials.*—*N*-Benzylidene-*p*-anisidines were from previous work.[1] *N*-Diphenylmethylene-*p*-anisidine, m.p. 78°, was prepared by a known method [12] and gave a correct analysis. Acetonitrile and sodium perchlorate were purified as described previously.[1] Pyridine was purified by a standard procedure. Picoline and lutidines from commercial sources were purified by distillation. Acetamide was also purified by distillation.

*Apparatus.*—Cyclic voltammetry and controlled potential electrolysis were carried out as described previously.[1,13] A Hitachi spectrophotometer, type 139, was used for u.v. spectroscopy. I.r. and n.m.r. spectra were obtained using a Hitachi ETI-G3 spectrophotometer and a Hitachi–Perkin-Elmer R-20A spectrometer, respectively.

*Controlled Potential Electrolysis.*—In each electrolysis, the background solution (acetonitrile containing 0·1M-sodium perchlorate and 1% pyridine) was subjected to pre-electrolysis at a potential of 0·05 V higher than that to be applied when substrate was added. Although a small current (usually <1% of the initial current observed when substrate was added) was observed in the initial part of the pre-electrolysis, the same behaviour was observed in the absence of pyridine.[1] This initial current reduced to a negligible size within 10 min both in the presence and absence of pyridine. The pre-electrolysis was continued for *ca.* 25 min. After pre-electrolysis, a weighed amount of substrate was added together with a small amount of acetonitrile, and the potential was adjusted. Electrolysis was continued until the value of current was <2% of the initial value. The current–time curve was recorded both during pre-electrolysis and the electrolysis of substrate. *n* Values were calculated from the quantity of electricity consumed during electrolysis, this being obtained from the area below the current–time curve.

When pre-electrolysis of acetonitrile containing 0·1M-sodium perchlorate and 1% pyridine was carried out at 1·80 V, a potential high enough to bring about the oxidation of pyridine itself (*cf.* Figure 1), a large current was observed during the first few minutes and then it decreased to a small constant value. After pre-electrolysis, substrate was added and the same steps as described above were carried out. In this case, however, oxidation of substrate hardly occurred, *i.e.* when the electrolysis was started a much smaller than expected current was observed. Severe filming of the electrode was observed. When the film was washed off and electrolysis was started again, oxidation proceeded normally. These findings indicate that, if considerable amounts of

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[10] L. Eberson and K. Nyberg, *Acta Chem. Scand.*, 1964, **18**, 1567.

[11] L. Eberson and K. Nyberg, *Tetrahedron Letters*, 1966, 2389.

[12] G. Reddelien, *Annalen*, 1912, **388**, 188.

[13] M. Masui, H. Sayo, and Y. Tsuda, *J. Chem. Soc.* (*B*), 1968, 973; M. Masui and H. Sayo, *ibid.*, 1971, 1593.

pyridine are oxidized, the product is strongly adsorbed on the electrode surface and further oxidation of pyridine and/or other substances is prohibited.

*Isolation of Products*.—Typical examples are described.

(a) N-(2-p-*Chlorobenzylideneamino-5-methoxyphenyl*)-*pyridinium perchlorate* (I; X = *p*-Cl). *N*-*p*-Chlorobenzylidene-*p*-anisidine (442 mg) was subjected to electrolysis at 1·15 V in acetonitrile (100 ml) containing 1% pyridine and 0·1M-$NaClO_4$ for 140 min at room temperature. *ca.* 398 Coulombs, corresponding to $n = 2{\cdot}30$, were consumed. The resulting brown solution showed essentially no first wave in the cyclic voltammogram (*cf.* Figure 1). The solution was evaporated to dryness under reduced pressure and the residue was washed with ethyl acetate (100 ml). The brown crystals obtained (1·03 g) were subjected to column chromatography on neutral alumina with acetonitrile as eluant. The yellow crystals obtained (516 mg) from the first effluent were recrystallized from methanol to give yellow needles which were identified as *N*-(2-*p*-chlorobenzylideneamino-5-methoxyphenyl)pyridinium perchlorate (I; X = *p*-Cl) by elemental analysis and i.r. and n.m.r. spectra (Table 4). A small amount of another material giving yellow crystals was obtained in later fractions of the effluent. This was recrystallized from methanol–chloroform–ether to give yellow needles and was identified as *N*-(2-amino-5-methoxyphenyl)-pyridinium perchlorate (VIII) [the free base of (II)] from its i.r. and n.m.r. spectra.

Increasing the pyridine concentration above 1% had little effect on the yield of (I). Electrolysis at a lower temperature, however, improved the yield, *e.g.* at 0—5 °C compound (I) was obtained almost quantitatively.

When compound (I; X = *p*-Cl) was hydrolysed in excess of aqueous hydrochloric acid solution, compound (II) and *p*-chlorobenzaldehyde were produced. Similarly (II) was obtained upon hydrolysis of the *p*-methoxy- and unsubstituted derivatives of (I). The p$K_a'$ value of (II) (1·32 ± 0·02), determined spectrophotometrically by the method of Reeves,[14,*] supports the suggested structure. The p$K_{a_1}'$ values of phenylenediammonium ion have been reported to be 1·3, 2·65, and 3·29 for the *ortho*-, *meta*-, and *para*-derivatives, respectively.[15]

TABLE 4

Physical and spectroscopic data of the products obtained on electrolysis

| Compound | M.p. (°C) | | Elemental analysis (%) | | | N.m.r.[a] [δ(p.p.m.)] | I.r.[b] (ν/cm⁻¹) |
|---|---|---|---|---|---|---|---|
| | | | C | H | N | | |
| (I; X = H) | 235 | | | | | 3·84 (3H, s) | 3120, 3070, 1630, 1510 |
| | | Found | 58·45 | 4·45 | 7·15 | 7·9—8·9 (5H, m) [c] | |
| | | Required | 58·7 | 4·4 | 7·2 | 8·71 (1H, s) | |
| | | | | | | 7·1—7·7 (8H, m) | |
| (I; X = *p*-OMe) | 215·5—217 | | | | | 3·81 (3H, s) | 3125, 3070, 1620, 1600, 1570, 1513 |
| | | | | | | 3·88 (3H, s) | |
| | | Found | 57·25 | 4·6 | 6·9 | 7·9—8·9 (5H, m) [c] | |
| | | Required | 57·35 | 4·55 | 6·7 | 8·64 (1H, s) | |
| | | | | | | 6·8—7·7 (7H, m) | |
| (I: X = *p*-Cl) | 261 | | | | | 3·86 (3H, s) | 3125, 3070, 1630, 1505 |
| | | Found | 53·8 | 3·9 | 6·6 | 7·9—8·9 (5H, m) [c] | |
| | | Required | 53·9 | 3·8 | 6·6 | 8·68 (1H, s) | |
| | | | | | | 7·1—7·7 (7H, m) | |
| (II) | 189—190 (decomp.) | | | | | 3·86 (3H, s) | 3100, 2830—2200, 1990—1930, 1606, 1564, 1504 |
| | | | | | | 8·1—9·2 (5H, m) [c] | |
| | | Found | 52·55 | 5·1 | 10·2 | 7·58 (1H, d) [d] (1) | |
| | | Required | 52·75 | 5·15 | 10·25 | 7·20—7·45 (2H, m) [d] | |
| | | | | | | 3·79 (3H, s) | |
| | | | | | | 8·1—9·0 (5H, m) [c] (2) | |
| | | | | | | 6·97—7·08 (3H, m) | |
| (VIII) | 172—174 | | | | | 3·79 (3H, s) | 3420, 3345, 3230, 3120, 3070, 1627, 1586, 1510 |
| | | Found | 48·35 | 4·2 | 9·1 | 8·1—9·0 (5H, m) [c] | |
| | | Required | 47·95 | 4·45 | 9·3 | 6·97—7·08 (3H, m) | |

[a] The n.m.r. spectrum of (I) was recorded in acetonitrile with $Me_4Si$ as internal standard, and those of (II)(1) and (VIII) in $D_2O$ and (II)(2) in $D_2O$–[$^2H_5$]pyridine with sodium 4,4-dimethyl-4-silapentanesulphonate as standard; 60 MHz. [b] For KBr discs. [c] These signals were assigned to the protons of the pyridinium group. In the case of (I; X = *p*-Cl) the assignment was based on substitution of [$^2H_5$]pyridine for pyridine. [d] The assignment was made by comparing the spectra obtained at 60 and 100 MHz.

(b) *Electrolysis of* N-*diphenylmethylene*-p-*anisidine*. *N*-Diphenylmethylene-*p*-anisidine (152 mg) was subjected to electrolysis as described above at 1·05 V for 260 min at 3 °C. The resulting deep red solution had the main peak at 1·39 V on cyclic voltammetry (*cf.* Table 1) and had essentially lost the original first wave, indicating that a pyridinated Schiff's base was formed as the main product. The solution was evaporated to dryness under reduced pressure, the residue was extracted with chloroform (100 ml), the solution was evaporated to dryness, again the residue was dissolved in excess of aqueous hydrochloric acid solution, and was warmed on a water-bath for 20 h. The solution was then evaporated to dryness under reduced pressure, the residue was washed with chloroform (20 ml), and was recrystallized from hydrochloric acid–acetonitrile to give brown needles (*ca.* 30 mg). This material was identified as compound (II) from its i.r. spectrum. The low yield may be attributed to losses in the work-up.

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[*] Compound (II) exhibited absorption maxima at 220 and 258 nm in strong acid solution, and at 232, 258, and 300 nm in neutral or alkaline solution. Its p$K_a'$ value was determined by measuring the change in absorbance at 300 nm with change in pH.

[14] R. L. Reeves, *J. Amer. Chem. Soc.*, 1962, **84**, 3332.
[15] R. Kuhn and F. Zumstein, *Ber.*, 1926, **59**, 488.