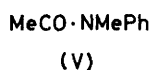
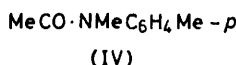
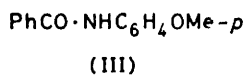
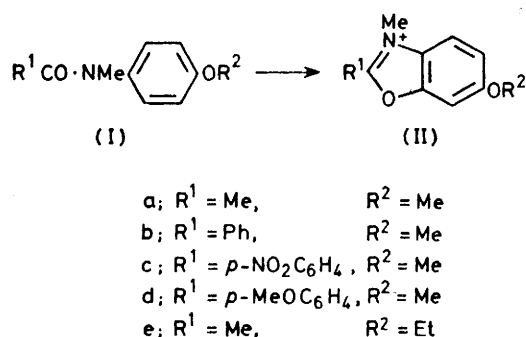


## Anodic Oxidation of Carboxamides. Part 3.<sup>1</sup> The Mechanism of Anodic Cyclization of *N*-Methylcarbanilides

By Hidenobu Ohmori, Chihiro Ueda, Yasuhiro Nobusue, Naoko Saitou, Tomoko Yokota, and Masai-chiro Masui,\* Faculty of Pharmaceutical Sciences, Osaka University, 1—6 Yamadaoka, Suita, Osaka-fu, Japan

Anodic oxidation in methanol of *N*-methylcarbanilides with an alkoxy-group *para* to the nitrogen atom (I) gives the intramolecular cyclization products, *N*-methylbenzoxazolium perchlorates: no cyclization product is obtained in the electrolysis of the anilides in acetonitrile. The process of cyclization was investigated by cyclic voltammetry, controlled potential electrolysis, and open circuit relaxation experiments using an optically transparent glassy carbon electrode. In spectroelectrochemical experiments on 4'-methoxy-*N*-methylbenzanilides (Ib—d) in methanol, accumulation of a metastable intermediate has been demonstrated. A possible reaction sequence for the formation of the benzoxazolium salts is discussed.

PREVIOUSLY we reported on the anodic oxidation of 4'-methoxy-*N*-methylbenzanilide (Ib) at a glassy carbon electrode.<sup>1,2</sup> On electrolysis of (Ib) in nominally dry acetonitrile or in acetonitrile with a small amount (<1%) of added water, *p*-benzoquinone and *N*-methylbenzamide were obtained as the main products.<sup>1</sup> On the other hand, electrolysis of (Ib) in methanol or in acetonitrile containing methanol (1%) resulted in the formation of 6-methoxy-3-methyl-2-phenylbenzoxazolium perchlorate (IIb).<sup>2</sup> In both cases a dication derived from (Ib) has been suggested to be formed by the initial apparent two-electron transfer from the substrate. However, the processes for the reactions of the dication with water and methanol to give the final products remain uncertain, and seem worthy of further investigation.



Tabaković *et al.* have reported that the anodic oxidation of thiobenzamides in acetonitrile gives benzothiazoles.<sup>3</sup> However, a detailed mechanistic study on the reaction seems not to have been performed, and preliminary experiments carried out by us<sup>2,†</sup> suggested

that the processes for the two seemingly similar cyclization reactions, benzoxazolium and thiazole formation, differ considerably from each other.

This paper reports the results of cyclic voltammetry and controlled potential electrolysis of (I) and 4'-methoxybenzanilide (III) in methanol at a glassy carbon electrode together with the results of a spectroelectrochemical study on an intermediate formed in the electrolysis using an optically transparent glassy carbon electrode. Also the process for anodic cyclization of (I) is discussed. The anilide (III) is included in the present study because it is structurally related to (Ib) and the results of electrolysis of (III) in acetonitrile<sup>4</sup> are similar to those for (Ib).

### RESULTS

Upon cyclic voltammetry in methanol containing 0.1M-sodium perchlorate, the anilide (Ib) showed two anodic peaks at 1.27 and 1.68 V. No cathodic peak was observed on a reverse scan down to -0.1 V. All potentials were measured against an aqueous saturated calomel electrode (s.c.e.). The peak potential and the peak current of the first anodic peak of (Ib) almost coincided with those obtained in acetonitrile under the same voltammetric conditions,<sup>1,†</sup> indicating that the initial electrode process of (Ib) in methanol corresponds to an apparent two-electron transfer to give a dication as suggested for the process in acetonitrile.<sup>1</sup> Similar voltammetric results were obtained for (Ia and c—e)

TABLE I

Voltammetric peak potentials (V *versus* s.c.e.) of the anilides (I) and (III) in methanol containing 0.1M-NaClO<sub>4</sub><sup>a</sup>

Compd.	(Ia)	(Ib)	(Ic)	(Id)	(Ie)	(III)
<i>E</i> <sub>p1</sub> <sup>b</sup>	1.30	1.27	1.40	1.25	1.35 <sup>d</sup>	1.19
<i>E</i> <sub>p2</sub> <sup>c</sup>	1.67	1.68	1.90	1.69	1.69 <sup>d</sup>	1.71

<sup>a</sup> At a glassy carbon electrode (geometric area 0.071 cm<sup>2</sup>); concentration of anilide, *ca.* 5mM; at 50 mV s<sup>-1</sup>. <sup>b</sup> First anodic peak. <sup>c</sup> Second anodic peak. <sup>d</sup> In ethanol containing 0.1M-NaClO<sub>4</sub>.

and 4'-methoxybenzanilide (III). The voltammetric results for (I) and (III) are summarized in Table I, and a typical voltammogram of (Ia) is shown in Figure 1.

† Anodic oxidation of benzanilide and 4'-methoxybenzanilide did not give cyclization products either in methanol or in acetonitrile.

‡ In acetonitrile the second anodic peak is absent.

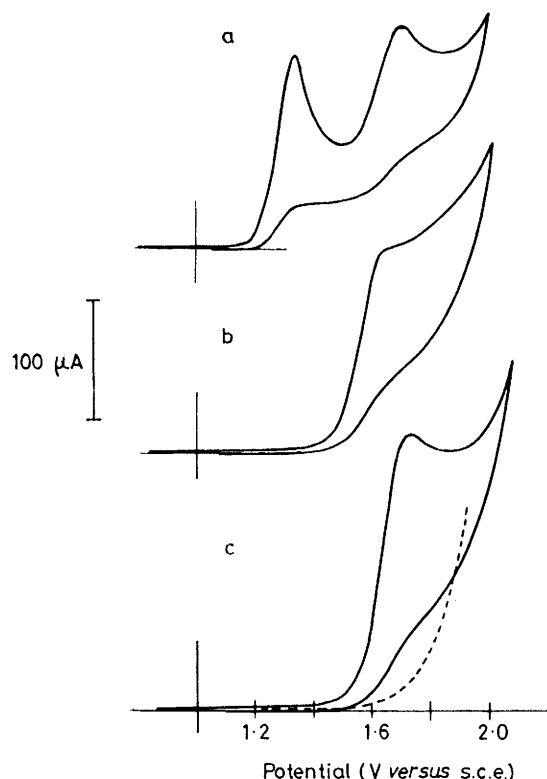


FIGURE 1 Cyclic voltammograms of (a) the anilide (Ia), (b) *N*-acetyl-*N*-methyl-*p*-toluidine (IV), and (c) *N*-methylacetanilide (V) in methanol containing 0.1M- $\text{NaClO}_4$  at a glassy carbon electrode (area  $0.071 \text{ cm}^2$ ): voltage sweep rate,  $50 \text{ mV s}^{-1}$ ; concentration of substrate, ca. 5mM. Dashed line represents the background current of the medium

Table 2 summarizes typical results for controlled potential electrolysis of the anilides (I) in methanol at the potential of the first anodic peak. The second anodic peaks of (I) were missing in the solution from electrolysis along with the first anodic peaks, indicating that the second anodic peak is

TABLE 2

Results of controlled potential electrolysis of the anilide (I) <sup>a</sup>

Compound (Amount/mmol)	Applied potential <sup>b</sup>	<i>n</i> Value	Yield of (II) (%)
(Ia) (2.68)	1.30	2.1	70
(Ib) (0.84)	1.27	2.2	73
(Ic) (0.71)	1.40	2.4	75
(Id) (0.80)	1.25	2.4	50
(Ie) (0.55) <sup>c</sup>	1.35	2.1	35

In methanol (100ml) containing 0.1M- $\text{NaClO}_4$  at a glassy carbon plate anode in an H-type divided cell; at  $0^\circ \text{C}$ . <sup>b</sup> V versus s.c.e. <sup>c</sup> In ethanol containing 0.1M- $\text{NaClO}_4$ .

due to the oxidation of some intermediate formed at the first anodic peak. The isolated benzoxazolium salts (II) showed no voltammetric oxidation peak under the conditions in which the cyclic voltammetry of the starting anilides (I) was performed. As described previously,<sup>1,2</sup> the benzoxazolium salts (II) were not detected in the solution from electrolysis of (I) in acetonitrile.

In order to see if cyclization products similar to (II) could be obtained with *N*-methylanilides without an alkoxy-group *para* to the nitrogen atom, *N*-acetyl-*N*-methyl-*p*-toluidine (IV) and *N*-methylacetanilide (V) were selected

and their electrochemical oxidation was studied briefly. On cyclic voltammetry in methanol, the anilides (IV) and (V) showed only one anodic peak (see Figure 1) in contrast to (Ia). In the electrolysis of (IV) and (V) in methanol at 1.55 and 1.65 V, respectively, neither a cyclization product nor any other stable product could be identified. In the case of (V), electrode filming was detected. These results suggest that under the present experimental conditions the benzoxazolium salt formation is limited to those anilides with an alkoxy-group *para* to the nitrogen atom.

When (Ia) was electrolysed in [ $^2\text{H}_4$ ]methanol (Merck; 99%  $^2\text{H}$ ), 75% of the methoxy-group on the phenyl ring of the resulting benzoxazolium salt was substituted for a  $\text{CD}_3\text{O}$  group.\* Electrolysis of (Ia) in ethanol gave a mixture of (IIa and e) in the ratio 1 : 9, i.e. 90% of the methoxy-group was replaced by an ethoxy-group. Similarly, electrolysis of (Ie) in methanol gave (IIa and e) in the ratio 7 : 3.

In the anodic oxidation of the anilide (Ib) in acetonitrile, the formation of *p*-benzoquinone and *N*-methylbenzamide was ascribed to the reaction of a dication derived from (Ib) with adventitious water.<sup>1</sup> A similar reaction of water was also conceivable as a side-reaction in the electrolysis of (I) in methanol. As shown in Table 3, the amount of *N*-

TABLE 3

Amount of  $\text{XC}_6\text{H}_4\text{CONHMe}$  formed on electrolysis of the anilides (Ib—d) (A) in methanol and (B) in methanol containing 10% (w/v) water <sup>a</sup>

Compound	X	% Yield <sup>b</sup> (A)	(B)
(Ib)	H	11	45
(Ic)	<i>p</i> - $\text{NO}_2$	3	29
(Id)	<i>p</i> -OMe	28	56

<sup>a</sup> The results in this Table were obtained in separate experiments from those in Table 2, but formation of (II) was confirmed by absorption spectroscopy (see Experimental section): electrolyses were carried out at  $0^\circ \text{C}$ ; volume of anolyte, 10 ml; supporting electrolyte, 0.1M- $\text{NaClO}_4$ ; amount of substrates, ca. 10 mg. <sup>b</sup> Determined by h.p.l.c.

methylbenzamides formed on electrolysis of three benzaniilides (Ib—d) in nominally dry methanol and in methanol containing 10% (w/v) water increased with increase in the electron-donating power of the substituents on the benzoyl moiety.

Electrolysis of (III) in acetonitrile with or without added water resulted in the formation of benzamide and *p*-benzoquinone as the main products.<sup>4</sup> On electrolysis of (III) in methanol, however, neither benzamide nor a cyclization product was formed, but methyl benzoate was formed in 65% yield: the electricity consumed in the electrolysis was more than 4 F per mole of the substrate, and intractable tars were formed in addition to the ester.

Open circuit relaxation experiments <sup>5</sup> using an optically transparent electrode (o.t.e.) were carried out for the oxidation of (Ib—d) and (III) in methanol to explore the nature of the second anodic peak. The reticulated vitreous carbon (r.v.c.) o.t.e. reported by Norveil and Mamantov <sup>6</sup> was modified to meet our experimental conditions (see Experimental section). For each of the three anilides (Ib—d), an intermediate was detected and its decay was accompanied by the formation of the corresponding cyclization product (II). A typical example of the spectral change is shown in

\* The methoxy-group of (IIa) remained unchanged when (IIa) in [ $^2\text{H}_4$ ]methanol was heated in a sealed ampoule at  $60^\circ \text{C}$  for 18 h.

Figure 2. Both the decay of the intermediate and the formation of (II) obeyed good first-order kinetics, and the following rate constants were obtained by monitoring the

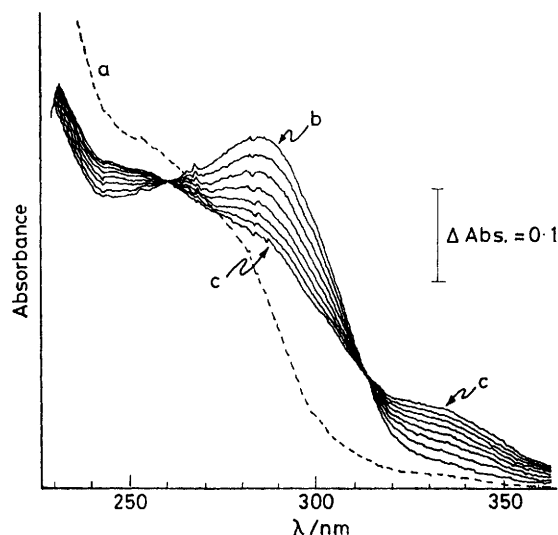


FIGURE 2 Absorption spectra of the anilide (Id) (*ca.* 0.2mm) in methanol containing 0.1M-NaClO<sub>4</sub> in the r.v.c.o.t.e. (Figure 4): (a) before electrolysis and (read from b to c) after 10, 40, 70, 100, 130, 160, 190, and 210 s from opening the circuit: electrolysis was allowed to proceed for 10 s at 1.60 V *versus* the silver plate (for detail, see Experimental section)

change of absorbance at a suitable wavelength (Figure 3): for the disappearance of the intermediate from (Ib),  $2.1 \times 10^{-2} \text{ s}^{-1}$  (monitored at 245 nm); (Ic),  $8.8 \times 10^{-2} \text{ s}^{-1}$  (270 nm); (Id),  $9.2 \times 10^{-3} \text{ s}^{-1}$  (285 nm); for the appearance of (IIb),  $2.5 \times 10^{-2} \text{ s}^{-1}$  (320 nm); (IIc),  $8.0 \times 10^{-2} \text{ s}^{-1}$  (340 nm); (IId),  $8.2 \times 10^{-3} \text{ s}^{-1}$  (340 nm). These rate constants were

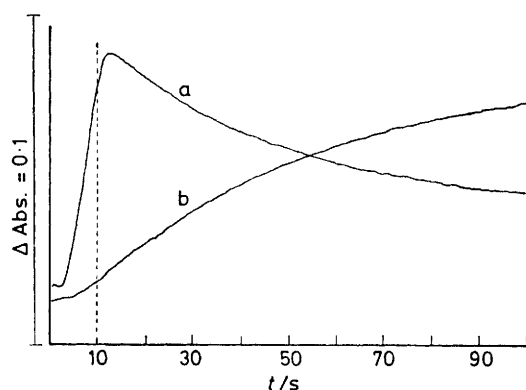
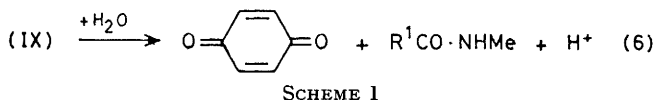
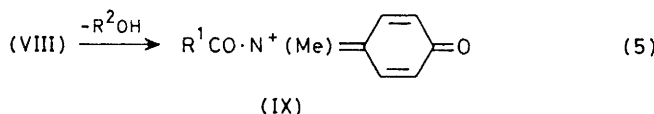
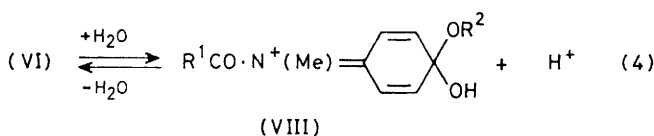
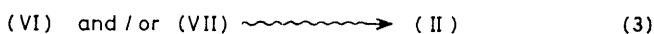
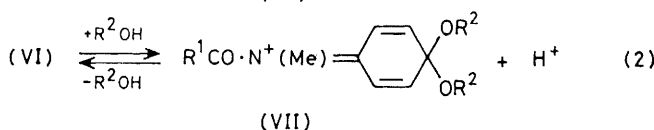
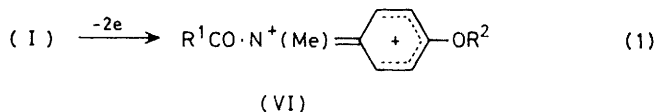


FIGURE 3 Absorption-time curves (a) for the generation and decay of the intermediate (see text) at 245 nm and (b) for the formation of (IIb) at 320 nm in the spectroelectrochemical experiment on the anilide (Ib) (*ca.* 0.2mm) in methanol containing 0.1M-NaClO<sub>4</sub> at 25 °C: electrolysis was allowed to proceed for 10 s (broken line) at 1.70 V *versus* the silver plate (for detail, see Experimental section)

correlated by the  $\sigma^+$  substituent constants with a  $\rho^+$  value of 0.66. Similar formation of an intermediate was also observed in the electrolysis of 4'-methoxybenzanilide (III), and a rate constant of  $2.6 \times 10^{-3} \text{ s}^{-1}$  (monitored at 242 nm) was obtained for the decay of the intermediate, which was accompanied by the formation of methyl benzoate.

## DISCUSSION

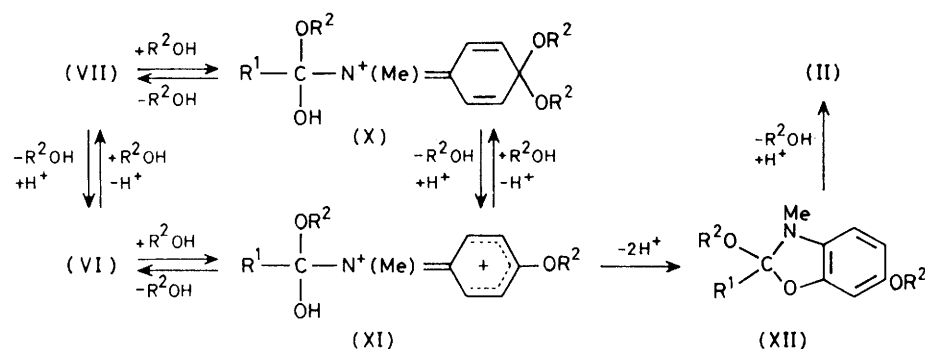
From the results on cyclic voltammetry and controlled potential electrolysis, the mechanism of anodic oxidation of the anilides (I) in methanol is described by Scheme 1, which also explains the results obtained for the oxidation of (Ib) in acetonitrile.<sup>1</sup> Since no conclusion can be drawn at present as to the details of the initial



electron transfer step, our discussion is limited to the reactions following the electron transfer.

In the cyclic voltammetry of anilides (I), the absence of any reduction peak due to the dication (VI) requires rapid follow-up reactions of the species. Two reactions can be considered, equilibria (2) and (4), which must lie far to the right. The exchange of an alkoxy-group during the course of the anodic cyclization can be explained by equilibrium (2). When water is present, the intermediate (VIII) can also be formed. The latter species will undergo further reaction to form *p*-benzoquinone and an *N*-methylcarboxamide *via* the quinone iminium ion intermediate (IX). In the anodic oxidation of 4'-methoxybenzanilide (III), an intermediate similar to (IX) has been demonstrated.<sup>4</sup> The predominant formation of *p*-benzoquinone and *N*-methylbenzamide from (Ib) in acetonitrile containing water<sup>1</sup> and the considerations below suggest that reaction (5) is fast enough to make equilibrium (4) essentially irreversible.

Although the mechanism of reaction (3) is not at once clear, Scheme 2 is suggested as one of the possibilities from the results in Table 3 and from the fact that methyl benzoate was the major product in the oxidation of (III) in methanol. If the anilides (Ib–d) react according to Scheme 1, the effects of substituents on the benzoyl ring



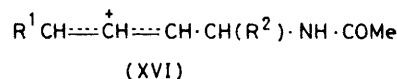
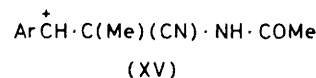
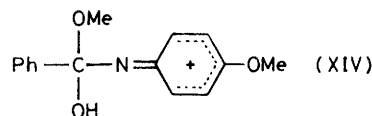
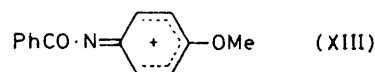
SCHEME 2

on the equilibrium constants for equilibria (2) and (4) are expected to be small and similar in magnitude. Thus if the benzoxazolium ions (IIb—d) were formed from (VI) and/or (VII) by attack of the carbonyl oxygen on the aniline ring without forming any intermediate, (I) with an electron-donating substituent on the benzoyl ring would give a better yield of (II) and, consequently, a smaller yield of the corresponding *N*-methylbenzamide in contrast to the results in Table 3. Participation of (X) and/or (XI) as transient intermediates, which is favoured by electron-withdrawing substituents, seems reasonable. The results of spectroelectrochemical experiments are also consistent with this view (see below). Formation of (II) *via* an intermediate such as (XII) is not unlikely. Compounds with structures similar to (XII) have been isolated in the reactions of 2,4-diamino-5-hydroxy-6-methylpyrimidine with benzoic anhydrides or with benzoyl chlorides, and have been shown to give the corresponding oxazolopyrimidines.<sup>7</sup>

Since the voltammetric behaviour of (III) is closely related to that of (Ib—d) (Table 1), similar reactions to those in Schemes 1 and 2 can be considered for the oxidation of (III) in methanol. In this case, however, the intermediates (VI) and (XI) will be replaced by (XIII)<sup>4</sup> and (XIV), respectively. Since (XI) is a dication and (XIV) is a monocation, cyclization of (XIV), if it were possible, would be slower than that of (XI) to give (XII); hence the decomposition of (XIV) to give methyl benzoate would become predominant.\* Another product from the decomposition is a nitrene or nitrenium ion which would undergo further reactions to give various electroactive species. The oxidation of these species may be responsible for the large coulometric *n* value and tarry products in the controlled potential electrolysis of (III) (see Results section). It is interesting to note that electrochemically generated carbonium ions such as (XV)<sup>9</sup> and (XVI)<sup>10</sup> give the corresponding oxazole derivatives probably without assistance by a nucleophile in contrast to that suggested in the present study. In the intermediates (VI) and (XIII), the electron deficiency

at the nitrogen atom would prevent unassisted cyclization of the species from occurring.

In the spectroelectrochemical experiments, an intermediate is accumulated rapidly after the beginning of electrolysis and then converted into the final product at a slower rate (see Figures 2 and 3). For a particular anilide the rate of decay of the intermediate is almost identical with that of formation of the final product, indicating that other intermediates, if they actually



exist, are all in the steady state concentration. Judging from the values of the rate constants obtained, the decay of the intermediate is negligible on the time scale of cyclic voltammetry. These results strongly suggest that the intermediate observed spectrophotometrically is the species responsible for the second anodic peak in the cyclic voltammetry of (I) in methanol.

The tetrahedral addition intermediates (X) and/or (XI), though their formation is required to explain the results of Table 3, cannot be the metastable species observed spectroscopically. Cyclization of (X) and/or (XI) will be accelerated by electron-donating substituents on the benzoyl ring in contrast to the observed results. Similar addition intermediates suggested in the hydrolysis of amides and imide esters are usually in the steady state.<sup>11</sup> On the other hand, intermediate (VII) may be taken as the dominant species. Rate-limiting attack of methanol on the carbonyl carbon of (VI) or (VII) to form the tetrahedral addition intermedi-

\* Breakdown of a tetrahedral addition intermediate such as (XIV) to give an ester can be regarded as a normal reaction. In the acid-catalysed hydrolysis of an imide ester, breakdown of the tetrahedral intermediate,  $R^1C(OH)(OR^2) \cdot NHR^3$ , usually produces an ester.<sup>8</sup> From this point of view the formation of (II) from (XI) might be a rather unusual reaction.



ates will be enhanced by electron-withdrawing substituents in the benzoyl ring,\* and the amount of *N*-methylbenzamide will decrease in the electrolysis of (Ib—d) in methanol containing water. The absence of the second anodic peak in acetonitrile with or without added water also supports the intervention of (VII). In acetonitrile containing water, the other intermediate (VIII) will be formed exclusively, and will be converted rapidly into the quinone iminium ion (IX) or further into *p*-benzoquinone and the corresponding amide. In the case of 4'-methoxybenzanilide (III) the intermediate (VII) with the methyl group on the nitrogen atom replaced by hydrogen is responsible for the second anodic peak in methanol. Since 4,4-dimethoxycyclohexa-2,5-dienone shows an anodic peak at 0.98 V in methanol<sup>15</sup> and (VII) is structurally related to the protonated form of the dienone, it is not improbable that the voltammetric peak of (VII) appears at *ca.* 1.7 V (see Table 1).

#### EXPERIMENTAL

**Materials.**—*N*-Methylcarbanilides (Ia—e) and (V) were prepared by acylation of *N*-methylanilides with acetic anhydride [(Ia,e) and (V)]<sup>16</sup> or with benzoyl chlorides [(Ib—d)].<sup>17</sup> The crude products were purified by distillation and/or recrystallization following chromatographic separation on silica gel. All compounds gave the expected analytical results. Commercial *N*-acetyl-*N*-methyl-*p*-toluidine (IV) was recrystallized from ether. 4'-Methoxybenzanilide (III) was prepared as described previously.<sup>4</sup> 4,4'-Dimethoxy-*N*-methylbenzanilide (Id), which is a new compound, had m.p. 60 °C (Found: C, 70.8; H, 6.3; N, 5.4. C<sub>16</sub>H<sub>17</sub>NO<sub>3</sub> requires C, 70.8; H, 6.8; N, 5.2%). Sodium perchlorate, used as supporting electrolyte, was recrystallized from ethanol–water and stored over phosphorus pentoxide under reduced pressure. Acetonitrile was distilled first from calcium hydride and then from phosphorus pentoxide after treatment by the method of Mann *et al.*<sup>18</sup> Methanol and ethanol were distilled before use.

**Apparatus.**—Cyclic voltammetry and controlled potential electrolysis were carried out as described previously.<sup>19</sup> All voltammetric measurements were carried out at 25 ± 0.05 °C. U.v., i.r., and n.m.r. spectra were obtained using Hitachi 124, EPI-2, and R-20A spectrometers, respectively. Spectroelectrochemical experiments were carried out using a Union Giken RA-601 stopped-flow, rapid-scan spectrometer connected with an RA-405 kinetic data processor, an RA-453 monitor scope, and an RA-452 X–Y recorder. A Hokuto Denko potentiostat–galvanostat was used to control the electrolysis with the r.v.c.o.t.e. The o.t.e. is constructed from quartz slides, a slice of r.v.c.<sup>6</sup> (RVC Product Co.; RVC 2 × 10–100-S), glassy carbon plate spacers, filter

paper, and a piece of silver plate (Figure 4). The whole edge of the o.t.e. was coated with epoxy resin. The use of glassy carbon spacers, which were mechanically connected to the r.v.c., improved the electrical contact between the electrode and external wires. The latter were connected to the spacers with conducting epoxy resin. The anode compartment of the o.t.e. had a cell volume of 90 µl, which was determined by the reported method,<sup>20</sup> and transmitted 45% of incident light (geometrical light path, 1.60 mm).

Typical examples of the spectroelectrochemical experiments are as follows. The o.t.e. was filled with a solution of the anilide (Id) (*ca.* 0.2mm) in methanol containing 0.1M-sodium perchlorate, and positioned in the thermo-controlled cell compartment of the spectrophotometer with a cell holder (Figure 4) fabricated from black epoxy resin.

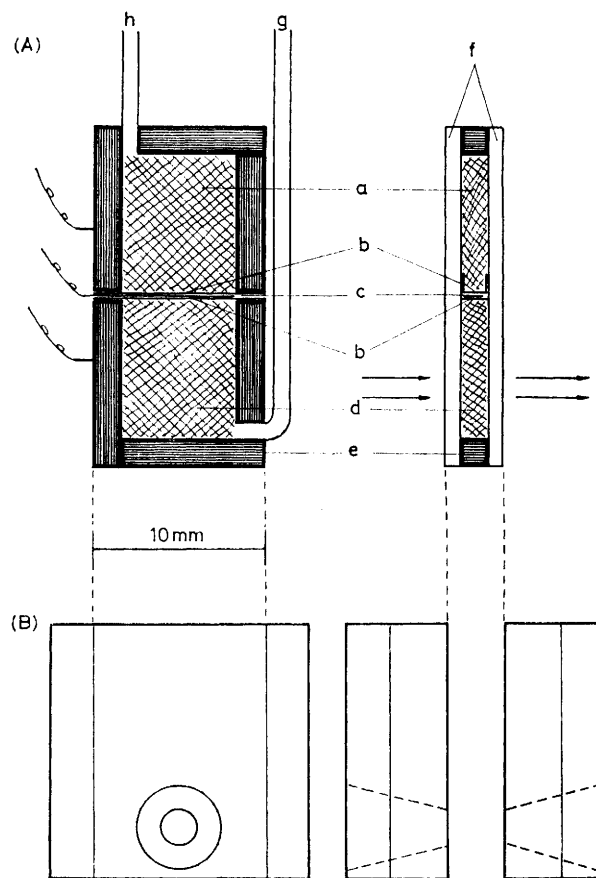


FIGURE 4 Front and side view of (A) the r.v.c.o.t.e. and (B) the cell holder; (a) r.v.c. cathode, (b) filter paper, (c) Ag plate reference electrode, (d) r.v.c. anode, (e) glassy carbon spacer, (f) quartz slide, (g) solution inlet, (h) solution outlet, and (i) light path: the o.t.e. is sandwiched between the cell holder

\* The first-order rate constants for the decay of the intermediates were correlated by the  $\sigma^+$  substituent constants but not by the Hammett  $\sigma$  values: the rate constants showed a convex relationship with the  $\sigma$  values. Most  $\rho^+$  values in  $\sigma^+$ – $\rho^+$  relationships hitherto reported are negative as expected from the origin of the relationship,<sup>12</sup> though some examples of positive  $\rho^+$  values can be found in the literature.<sup>13</sup> So it seems rather hard to explain the positive  $\rho^+$  value explicitly in terms of the rate-determining attack of methanol on (VI) or (VII). Another possibility is that the rate constants should be correlated by the  $\sigma$  values and the convex relation represents a change in the rate-determining step as observed in benzaldehyde semicarbazone formation.<sup>14</sup> Whichever explanation is true, however, the observed results do not support (X) and/or (XI) as a metastable intermediate.

After the thermal equilibrium was attained, the solution was electrolysed at 1.60 V *versus* a silver plate reference electrode for 10 s. The absorption spectra were obtained every 30 s (sampling time, 640 ms for 90 nm) after 10 s from opening the circuit. The electrolysis potential, electrolysis period, time lapse before monitoring the spectra, time intervals between successive measurements, and sampling time were dependent on the anilide used. In other runs with the same substrate, changes of absorbance were monitored continuously during electrogeneration and follow-

up reaction of the intermediate at the appropriate wavelength (see Figure 3).

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

(a) The anilide (Ia) (480 mg) was subjected to electrolysis in methanol (100 ml) containing 0.1M-NaClO<sub>4</sub> at 1.30 V at 0 °C until the value of current became <2% of the initial value. From the current-time curve, 543 C, which corresponded to *n* 2.1, were found to be consumed: this was also checked with a Hokuto Denko HF-102 coulometer. When the solution from the electrolysis was chilled, needles (520 mg) were obtained, some of which had already deposited during electrolysis. After recrystallization from methanol the product was identified as 6-methoxy-2,3-dimethylbenzoxazolium perchlorate (IIa), m.p. 172–173 °C (Found: C, 43.4; H, 4.4; N, 5.2. C<sub>10</sub>H<sub>12</sub>ClNO<sub>6</sub> requires C, 43.3; H, 4.4; N, 5.05%);  $\nu_{\max}$  (Nujol) 1 650, 1 620, and 1 090 cm<sup>-1</sup>;  $\lambda_{\max}$  (MeOH) 288 nm ( $\epsilon$  9 800);  $\delta$ (CD<sub>3</sub>CN) 2.96 (3 H, s, CMe), 3.91 (3 H, s, OMe), 3.99 (3 H, s, N<sup>+</sup>Me), and 7.2–7.9 (3 H, m, ArH). In another experiment, (Ia) (33 mg) was subjected to similar electrolysis in [2H<sub>6</sub>]methanol (5 ml). The anolyte was condensed to half of its original volume under reduced pressure, and then chilled to give needles. The n.m.r. spectrum of the product indicated that it was a mixture of (IIa) and the OCD<sub>3</sub> analogue in the ratio 1 : 3.

The following benzoxazolium salts were obtained similarly. 6-Methoxy-3-methyl-2-phenylbenzoxazolium perchlorate (IIb) had m.p. 196 °C (Found: C, 52.8; H, 4.2; N, 4.3. C<sub>15</sub>H<sub>14</sub>ClNO<sub>6</sub> requires C, 53.0; H, 4.15; N, 4.1%);  $\nu_{\max}$  (Nujol) 1 645, 1 610, and 1 100 cm<sup>-1</sup>;  $\lambda_{\max}$  (MeOH) 249 ( $\epsilon$  6 700) and 320 nm (9 600);  $\delta$ (CD<sub>3</sub>CN) 3.97 (3 H, s, OMe), 4.22 (3 H, s, N<sup>+</sup>Me), and 7.2–8.3 (8 H, m, ArH). When (IIb) was treated with aqueous sodium hydrogencarbonate followed by neutralization, extraction with chloroform, and evaporation of the chloroform under reduced pressure, N-(2-hydroxy-4-methoxyphenyl)-N-methylbenzamide was obtained, which was recrystallized from benzene as needles, m.p. 144–145 °C (Found: C, 70.3; H, 5.9; N, 5.4. C<sub>15</sub>H<sub>13</sub>NO<sub>3</sub> requires C, 70.0; H, 5.9; N, 5.4%); *m/e* 257 (*M*<sup>+</sup>);  $\nu_{\max}$  (Nujol) 1 610, 1 570, 1 500, and 1 160 cm<sup>-1</sup>;  $\delta$ (CD<sub>3</sub>CN) 3.21 (3 H, s, NMe), 3.66 (3 H, s, OMe), 6.22 (1 H, dd, *J* 1.2 and 8 Hz, ArH *para* to OH), 6.37 (1 H, d, *J* 1.2 Hz, ArH *ortho* to OH), 6.88 (1 H, d, *J* 8 Hz, ArH *meta* to OH), 7.1–7.4 (5 H, m, ArH), and 7.43 (1 H, s, OH). The formation of this amide further supports the structure of (IIb). 6-Methoxy-3-methyl-2-p-nitrophenylbenzoxazolium perchlorate (IIc) had m.p. 215–220 °C (Found: C, 46.95; H, 3.5; N, 7.8. C<sub>15</sub>H<sub>13</sub>ClN<sub>2</sub>O<sub>8</sub> requires C, 46.8; H, 3.4; N, 7.3%);  $\delta$ (CD<sub>3</sub>CN) 3.96 (3 H, s, OMe), 4.22 (3 H, s, N<sup>+</sup>Me), 7.3–8.0 (3 H, m, ArH), and 8.2–8.7 (4 H, m, ArH). 6-Methoxy-3-methyl-2-p-methoxyphenylbenzoxazolium perchlorate (IId) had m.p. 213–214 °C (Found: C, 52.0; H, 4.4; N, 4.1. C<sub>16</sub>H<sub>16</sub>ClNO<sub>7</sub> requires C, 52.0; H, 4.4; N, 3.8%);  $\delta$ (CD<sub>3</sub>CN) 3.91 (3 H, s, OMe), 3.94 (3 H, s, OMe), 4.14 (3 H, s, N<sup>+</sup>Me), and 7.1–8.2 (7 H, m, ArH). 6-Ethoxy-2,3-dimethylbenzoxazolium perchlorate (IIe) had m.p. 172–173 °C (Found: C, 45.0; H, 4.7; N, 4.9. C<sub>11</sub>H<sub>14</sub>ClNO<sub>6</sub> requires C, 45.3; H, 4.8; N, 4.8%);  $\delta$ (CD<sub>3</sub>CN) 1.42 (3 H, t, *J* 7 Hz, CH<sub>2</sub>Me), 2.93 (3 H, s, CMe), 3.99 (3 H, s, N<sup>+</sup>Me), 4.16 (2 H, q, *J* 7 Hz, CH<sub>2</sub>Me), and 7.1–7.8 (3 H, m, ArH).

(b) **Determination of N-methylbenzamides in the electrolysis of (Ib–d) (see Table 3).** The anilides (*ca.* 10 mg) were subjected to electrolysis in 10 ml of methanol or methanol containing 10% (w/v) water at appropriate potentials (see

Table 2) at 0 °C as described in (a). The solution from electrolysis was adjusted to 20.0 ml in a volumetric flask with methanol, and a part of the resulting solution was subjected to liquid chromatography to estimate the yield of the corresponding N-methylbenzamide by using a Waters 6000-A solvent delivery system with a U6K universal injector and a JASCO UVIDEK-1 spectrophotometer [Bondapak C<sub>18</sub> Corasil (37–50  $\mu$ m);  $\frac{1}{8} \times 2$  ft column; water–methanol–acetic acid (87 : 10 : 3); 1 ml min<sup>-1</sup>; 235 nm]. The remainder of the solution, after being diluted ten-fold with methanol, was used to confirm the formation of (II) spectrophotometrically. In the electrolysis of (Ic and d) carried out in the aqueous methanol, the amount of (IIc) was smaller than expected and (IId) was not detected, and the coulometric *n* values were considerably larger than two [3.8 for (Ic) and 4.0 for (Id)]. This is probably because (IIc and d) underwent a fairly rapid ring-opening reaction to the corresponding N-(2-hydroxy-4-methoxyphenyl)-N-methylbenzamides, which are oxidised more easily than the starting anilides. The half-life for the decomposition of (IId) was <10 min in methanol containing 10% water and a small amount of perchloric acid (a proton is liberated in the electrolysis).

(c) 4'-Methoxybenzanilide (III) (18.8 mg) was subjected to electrolysis in methanol (15 ml) containing 0.1M-NaClO<sub>4</sub> at 1.20 V at 0 °C. The coulometric *n* value was 5.8. The solution from electrolysis was adjusted to 25.0 ml with methanol in a volumetric flask, and the resulting solution was analysed by g.l.c., which was carried out by using a Nihondenshi JGC-20K gas chromatograph connected to a Takeda Riken TR-2215A digital integrator (packing, PEG-20M; 170 °C). Methyl benzoate was formed in 65% yield. Other products from the electrolysis were intractable tarry materials which could not be identified.

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