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Anodic Oxidation of Imidate Esters

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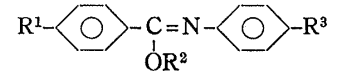
Anodic oxidation of several imidate esters (I) was investigated at a glassy carbon electrode in acetonitrile. On cyclic voltammetry, I showed one, two, or three anodic peaks depending upon the structure. Controlled potential electrolysis of methyl N-*p*-methoxyphenylbenzimidate (Ic) at the potential of the first anodic peak gave *p*-benzoquinone and methylbenzoate, together with the protonated starting material. Electrolysis of Ic and methyl N-phenylbenzimidate (Ia) in the presence of excess pyridine gave pyridinated imidate esters in which the pyridinium group is attached to the aniline ring. An intramolecular cyclization reaction to form spirodienones was observed on electrolysis, in the presence of perchloric acid, of aryl N-*p*-methoxyphenylbenzimidates with aryl groups of low oxidation potential (Ie—g). Possible mechanisms for the reactions are discussed.

Keywords——cyclic voltammetry; controlled potential electrolysis; imidate esters; anodic pyridination; intramolecular cyclization; 1,3-oxazines

We have previously reported the anodic oxidation of N-benzylidene-*p*-anisidines[1] and 4′-methoxybenzanilides.[2] Although the initial electron transfer involves the lone pair of electrons on the anisidine nitrogen atom in both series of compounds, the results of electrolysis in nominally dry acetonitrile are considerably different in the two cases. Electrolysis of the Schiff bases gives the protonated starting materials after consuming about 1 F per mol of the substrates. No other stable product could be identified. In the case of the anilides, *p*-benzoquinone and the corresponding benzamides are formed as the main products with coulometric *n*-values of about two. Since imidate esters of type I are structurally related to both the Schiff bases and the anilides, investigation of the electrochemical oxidation of I is expected to afford a clue not only to the difference in the electrochemical behavior of the Schiff bases and the anilides but also to the mechanistic ambiguity left in the previous studies.[1,2]



	R^1	R^2	R^3
Ia	H	Me	H
Ib	MeO	Me	H
Ic	H	Me	MeO
Id	H	Ph	MeO
Ie	H	3-MeO-C_6H_4	MeO
If	H	3,5-$(MeO)_2C_6H_3$	MeO
Ig	H	2-naphthyl	MeO

Chart 1

This paper reports the results of cyclic voltammetry and controlled potential electrolysis of I in acetonitrile at a glassy carbon electrode. New oxazine derivatives were obtained on electrolysis of Ie—g through intramolecular coupling.

Results

Cyclic Voltammetry

In acetonitrile containing 0.1 M sodium perchlorate, the imidate esters (I) showed one, two, or three anodic peaks in the range of 0—2.0 V *vs.* S.C.E. depending upon the substituents R^2 and R^3: the potentials of the observed peaks are summarized in Table I. No cathodic peak was observed down to −0.1 V in the reverse scan. The peak current of the first anodic

Table I. Voltammetric Peak Potentials (V *vs.* S.C.E.) of I[a)]

Compound	E_{p1}	E_{p2}[b)]	E_{p3}[b)]
Ia	1.35	—	—
Ib	1.33	—	—
Ic	1.05	1.75	—
Id	1.10	1.78	—
Ie	1.08	1.78	2.00
If	1.05	1.75	1.95
Ig	1.10	1.70	2.00
N-Benzylidene-*p*-anisidine	1.15	1.80	—

a) In acetonitrile containing 0.1 M $NaClO_4$ at a glassy carbon electrode (area=0.071 cm^2); at 50 mV s^{-1}.
b) The peak potential seems to be sensitive to small amounts of water contaminating the medium.

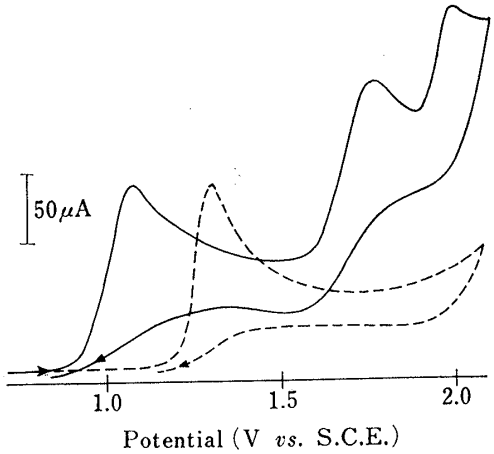


Fig. 1. Cyclic Voltammograms of Ia (8 mM) (dashed line) and Ie (8 mM) (solid line)

In acetonitrile containing 0.1 M $NaClO_4$; glassy carbon anode (area=0.071 cm^2); voltage sweep rate, 50 mV s^{-1}.

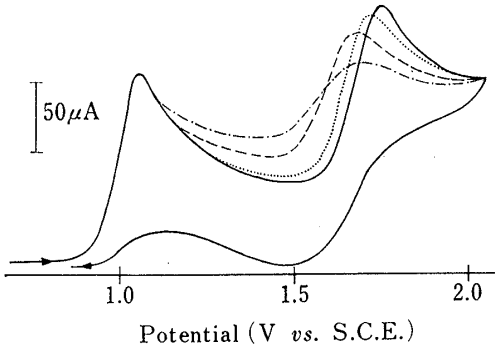


Fig. 2. Cyclic Voltammograms of Ic (8 mM)

In acetonitrile containing 0.1 M $NaClO_4$: ——, without added water; ·····, with 0.5% water; – – –, with 1% water; and —·—·—, with 3% water. Glassy carbon anode (area=0.071 cm^2); voltage sweep rate, 50 mV s^{-1}. Current voltage curves on the reverse scan for those with added water are not shown.

wave of I was similar in magnitude to that of N-benzylidene-*p*-anisidine,[1)] which corresponds to an apparent one-electron process.[1,3)] Typical voltammograms are shown in Figs. 1 and 2.

The effect of added acid and base on the cyclic voltammetry of I was examined. In the presence of perchloric acid, the first anodic wave decreased while the second wave (Ic—g) increased. With excess of the acid the first wave completely disappeared and the second wave shifted to less positive potentials by 100—200 mV (not shown). When pyridine was present the first wave increased, the second wave decreased, and a new peak appeared between the two waves. The new peak must be due to the oxidation of the pyridinated product (see Table II, run Nos. 3 and 4). With excess pyridine the peak current of the first wave was nearly twice as large as that observed in the absence of the base. 2,6-Lutidine, a hindered base, enhanced the first anodic wave as effectively as pyridine. The voltammetric behavior of I thus observed is quite similar to that of N-benzylidene-*p*-anisidine.[1,4)]

Fig. 2 illustrates the effects of water on the voltammogram of Ic. The first anodic wave was almost independent of added water when the concentration of water was less than 3%, while the second wave shifted slightly to less positive potentials and its peak height decreased. This change of the second wave was accompanied by the development of a small cathodic peak at around 0.2 V in the reverse scan. The latter peak is probably due to the reduction

of *p*-benzoquinone or its precursor, *p*-benzoquinoneimine, formed in the anodic scan (see Table II, run No. 2).[1)]

Controlled Potential Electrolysis

Table II summarizes typical results of controlled potential electrolysis of I in acetonitrile under various conditions. Some of the electrolysis products are shown in Chart 2. Severe electrode filming prevented the electrolysis of Ia and b with and without added water.

TABLE II. Results of Controlled Potential Electrolysis of I[a)]

Run No.	Compound (Amount/mg)	Additives (%, v/v)	Applied potential[b)]	*n*-Value	Products identified[c)] (Yield/%)
1	Ic(100)	None	1.05	1.05	IcH^+(50), Q(27), BzOMe(38)
2	Ic(100)	H_2O(0.5)	1.05	1.1	IcH^+(48), Q(42), BzOMe(47)
3	Ic(150)	Pyridine (1)	1.05	2.0	II (44)[d)]
4	Ia(150)	Pyridine (1)	1.40	1.7[e)]	III (28)[d)]
5	Ic(120)	70% $HClO_4$ (1)	1.45	2.1	Q(85), BzOMe (95)
6	Id(130)	70% $HClO_4$ (1)	1.45	2.1	Q (35), BzOPh (48)[f)]
7	Ie(130)	70% $HClO_4$ (1)	1.45	1.8	IVe (63)
8	If(130)	70% $HClO_4$ (1)	1.45	2.0	IVf (67)
9	Ig(130)	70% $HClO_4$ (1)	1.45	2.0	IVg (78)

a) In acetonitrile (40 ml) containing 0.1 M $NaClO_4$ at a glassy carbon plate anode in an H-type divided cell; electrolysis was carried out at room temperature (run Nos. 1—4) or at 0° (run Nos. 5—9).
b) V *vs.* S.C.E.
c) IcH^+: protonated form of Ic . Q: *p*-benzoquinone.
d) Isolated yield after recrystallization.
e) Electrode filming was observed.
f) No other stable product was detected.

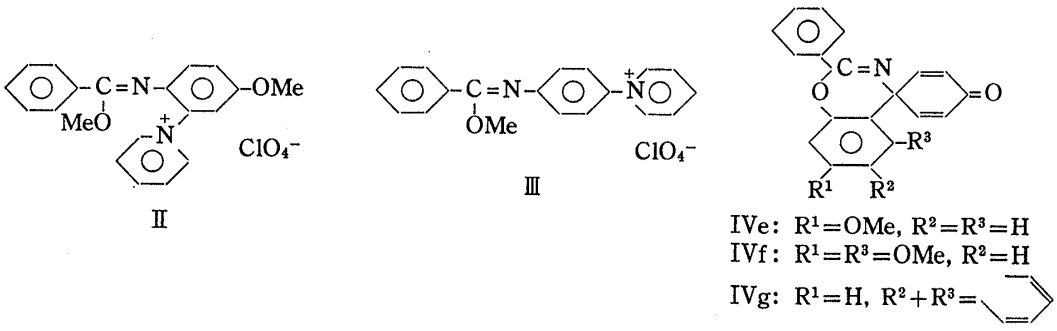


Chart 2

Electrolysis of Ic without an additive gave *p*-benzoquinone and methylbenzoate in addition to the protonated starting material (run No. 1) in contrast to the results previously obtained on N-benzylidene-*p*-anisidine.[1)] On the other hand, the results of electrolysis of Ic in the presence of excess pyridine (run No. 3) are essentially the same as those for N-benzylidene-*p*-anisidines under the same conditions.[4)] In the presence of perchloric acid, electrolysis of I with R^2 of relatively low oxidation potential[5)] (Ie—g) gave spirodienones (IV) through intramolecular cyclization.

Discussion

The peak potential of the first anodic wave of I is little affected by the substituents R^1 and R^2 (*cf.* E_{p1} values for Ia and b, and Ic—g in Table I), while change in R^3 has a considerable effect on the peak potential (*cf.* E_{p1} value for Ia and c). These results, together with the close similarity of the E_{p1} and E_{p2} values of Ic—g to those of N-benzylidene-*p*-anisidine (see Table I), suggest that the initial electron transfer in I involves the lone pair electrones on the nitrogen

atom, which must conjugate with the aniline part of the molecule as in the case of N-benzylideneanilines.[6]

In the anodic oxidation of N-benzylideneanilines in dry acetonitrile, two mechanisms have been suggested for the reaction of the initially formed N-benzylideneaniline cation radical, Ar–CH=N$^{+\cdot}$–Ar′, to form the protonated starting Schiff base.[1,3,7] One involves transfer of one proton and one electron from the cation radical to the unoxidized starting Schiff base and to the electrode, respectively, to give the protonated Schiff base and the N-benzylidyneanilinium cation, Ar–C≡N$^+$–Ar′.[3,7] In the other mechanism, which has been suggested by analogy with that for the oxidation of aliphatic amides,[8] the cation radical abstracts a hydrogen atom from the solvent to give the protonated Schiff base and the radical, $\cdot CH_2CN$: the latter radical may dimerize to form succinonitrile.[8] However, no product other than the protonated Schiff base has been proved to be formed.[1,3,7] In the oxidation of I, formation of a cation such as N-benzylidyneanilinium ion is improbable, and succinonitrile was not detected in the electrolysis solution. Thus, the reactions suggested for the N-benzylideneaniline cation radical are not applicable to the protonation of I under the present experimental conditions.

The results of electrolysis of Ic with and without added water (Table II, run Nos. 1 and 2) suggest that the acetonitrile used was contaminated with a small amount of water.[1,2] Though the detailed mechanism is not yet clear, Chart 3 shows a plausible process for the protonation of Ic. The lower yield of methylbenzoate and *p*-benzoquinone on electrolysis without added water are probably due to incomplete hydrolysis of some intermediate formed by the second electron transfer.

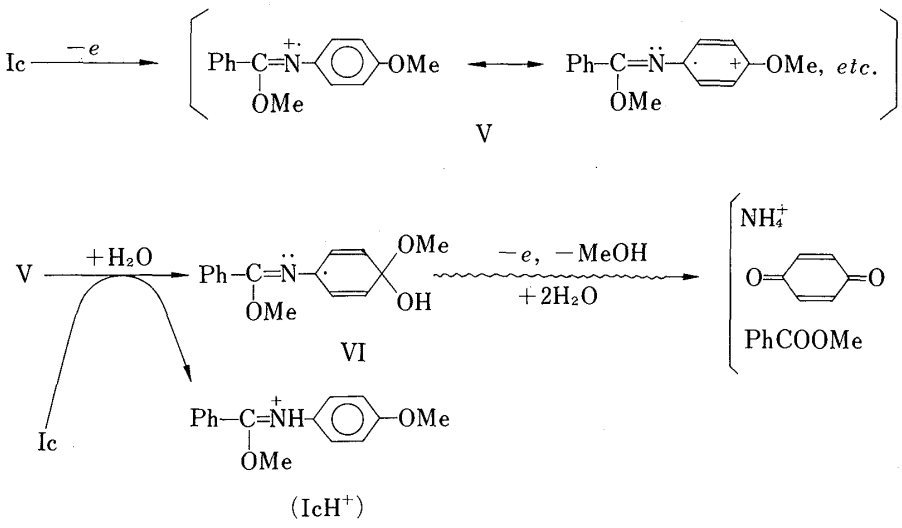


Chart 3

The pyridinated products II and III could be formed by a path like that proposed for the anodic pyridination of N-benzylidene-*p*-anisidines: the fate of the N-benzylidene-*p*-anisidine cation radical formed by initial one-electron transfer was suggested to involve proton transfer to pyridine from the anisidine ring *ortho* to the nitrogen atom followed by further one-electron transfer and attack of pyridine on the anisidine ring.[4] Though the present results do not necessarily rule out such a mechanism, Chart 3 suggests another reaction sequence for the cation radical of I: nucleophilic addition of pyridine on the anisidine ring followed by further one-electron transfer and loss of a proton.[9] A similar process has been suggested in the anodic pyridination of aromatic hydrocarbons.[10] At present, no definite conclusion can be reached as to which of the two mechanisms is actually the case.[9]

The intramolecular cyclization of Ie—g can be included in the family of widely studied intramolecular oxidative coupling reactions of alkoxy aromatic compounds, usually derivatives of biphenyl.[11,12] The mechanisms suggested for the reactions may be divided for convenience

into two types: two successive one-electron transfers from the substrate to give a dication diradical, followed by coupling (an eec mechanism[11]), and attack of a cation radical moiety formed by initial one-electron transfer upon an unoxidized aromatic ring followed by further one-electron transfer (an ece mechanism[11]). Which of the two mechanisms is operative and the precise course of the reaction seem to depend on the structure of the particular substrate and on the experimental conditions. In the case of I, cyclization from the corresponding cation radical (*cf.* V in Chart 3) is improbable because electrolysis of Ie—g in acetonitrile at the potential of the first anodic wave did not give the cyclization products.[13]

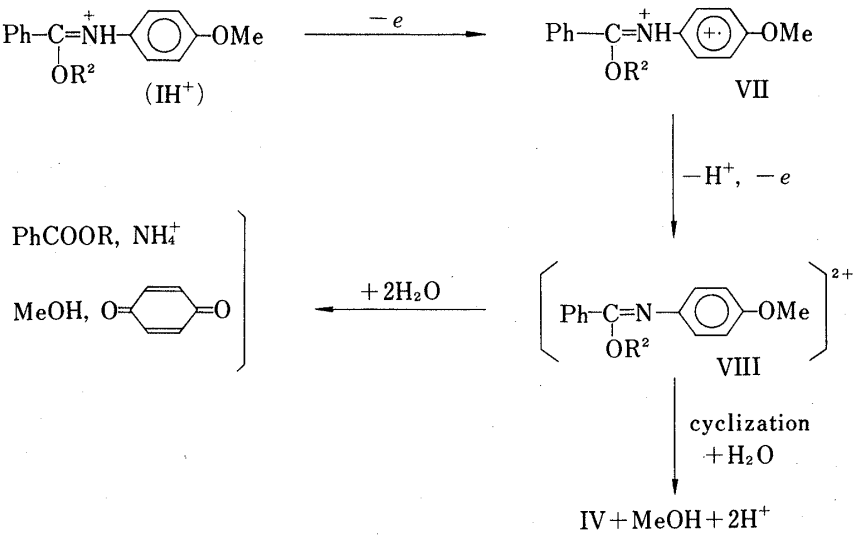


Chart 4

The pathway shown in Chart 4 is suggested for the electrolysis of I in acetonitrile containing perchloric acid. A process involving cyclization of the radical dication (VII) followed by deprotonation and further electron transfer might be considered. Such a process has been demonstrated in the coupling of laudanosin in acidic acetonitrile and cooresponds to the ece mechanism.[11] However, the radical dication (VII) must be a very strong acid because the proton is attached to the dicationic center; and hence any reaction preceding the deprotonation of VII seems unlikely.

Two forms can be considered for the dication (VIII) derived from Ie—g: a species with two positive charges on the anisidine part of the molecule and a dication diradical, Ph–C(OAr)$^{+\cdot}$ = N–(C_6H_4OMe)$^{+\cdot}$.[14] Cyclization from the latter species corresponds to the eec mechanism demonstrated in the cyclization of 3,3′,4-trimethoxybibenzyl.[15] Which of the two species undergoes cyclization is difficult to deduce from the present results.

In Chart 4, the initial electron transfer is assumed to occur from the anisidine part of the molecule. This assumption should be correct at least for Ic and d, because *p*-anisidine shows a broad anodic peak at 1.65 V in acetonitrile containing perchloric acid (the discharge of *p*-anisidinium ion begins at around 1.0 V). However, for Ie—g initial electron transfer from the aryloxy part of the molecule also seems feasible (see footnote 14). If this is the case, the most probable process is the formation of a cation radical on the aryloxy ring, deprotonation and further electron transfer from the anisidine part, and coupling of the resulting dication diradical.

Experimental

Materials——The imidate esters (I) were prepared by known methods[16] and gave the expected analytical results: the mp's or bp's are Ia, 135° (10 mmHg) [lit.[16a] 157—158° (12 mmHg)]; b, 260° (5 mmHg); c, 150° (5 mmHg); d, 97° (lit.[17] 97.5—99°); e, 59°; f, 82°; g, 112°. Sodium perchlorate was purified as described

previously.[1] Acetonitrile was distilled first from calcium hydride and then from phosphorus pentoxide after treatment by the method of O'Donnell *et al.*[18]

Apparatus——Cyclic voltammetry and controlled potential electrolysis were carried out as described previously.[1] UV, IR, NMR, and mass spectra were obtained on Hitachi 124, EPI-2, R-20A, and RMU-6E spectrometer, respectively. GLC was carried out using a Nihondenshi JGC-20K gas chromatograph: PEG 200 was used as packing. HPLC was carried out using a Waters 6000-A solvent delivery system with a U6K universal injector and a JASCO UVIDEC-1 spectrophotometer; Bondapack C_{18}-Corasil and 60% aqueous methanol were employed.

Controlled Potential Electrolysis and Identification of Products——Typical examples of the procedure are described below. A glassy carbon plate anode was used throughout.

a) The imidate ester (Ic) (100 mg) was subjected to electrolysis in acetonitrile (40 ml) containing 0.1 M $NaClO_4$ at 1.05 V at room temperature until the value of the current fell below 2% of the initial value. From the current-time curve, 42.1 C, which corresponds to $n=1.05$, was found to have been consumed. A cyclic voltammogram of the electrolyzed solution lacked the first anodic peak of Ic (see Fig. 2) and showed an anodic peak which corresponds to the second anodic peak of the substrate. When excess pyridine was added, the solution showed anodic peaks which coincide with those of Ic in acetonitrile with excess base. These results, together with those of HPLC analysis of the electrolyzed solution, indicate the formation of protonated starting material. A little of the electrolyzed solution was used to estimate the yield of Ic (HPLC), *p*-benzoquinone (HPLC), and methylbenzoate (GLC).

b) Ic (150 mg) was subjected to electrolysis in acetonitrile (40 ml) containing 0.1 M $NaClO_4$ and 0.4 ml of pyridine at 1.05 V. The electrolyzed solution was evaporated to dryness under reduced pressure and the residue was extracted with chloroform (3×30 ml). After removal of the chloroform under reduced pressure, the residue was subjected to column chromatography on neutral alumina first with chloroform and then with acetonitrile. The yellow crystals obtained from the acetonitrile effluent were recrystallized from methanol to give yellow needles (115 mg), which were identified as 1-(2-α-methoxybenzylideneamino-5-methoxyphenyl)pyridinium perchlorate (II); mp 172°. *Anal.* Calcd for $C_{20}H_{19}ClN_2O_6$: C, 57.35; H, 4.55; N, 6.70. Found: C, 57.01; H, 4.67; N, 6.68. IR ν_{max}^{Nujol} cm^{-1}: 3200, 3150, 1670, 1510, 1100. NMR (DMSO-d_6) δ: 3.70 and 3.85 (6H, two singlets, $-OC\underline{H}_3$), 6.65—7.50 (8H, multiplet, Ar–H), 8.10—9.20 (5H, multiplet, pyridinium ring-H). Compound II was hydrolyzed in dilute hydrochloric acid (*ca.* 2 hr). The resulting solution, after being washed with benzene, was evaporated to dryness under reduced pressure. The residue was recrystallized from hydrochloric acid–acetonitrile–ether to give light brown needles, which were identified as 4-methoxy-2-pyridiniumanilinium dichloride (mp 189° dec.) by comparing the spectral data with those of an authentic sample.[4]

1-(4-α-Methoxybenzylideneaminophenyl)pyridinium perchlorate (III) was obtained similarly as pale yellow needles (76 mg from 150 mg of Ia); mp 145°. *Anal.* Calcd for $C_{19}H_{17}ClN_2O_5$: C, 58.69; H, 4.38; N, 7.21. Found: C, 58.22; H, 4.37; N, 7.34. IR ν_{max}^{Nujol} cm^{-1}: 3150, 1660, 1600, 1100. NMR (DMSO-d_6) δ: 3.98 (3H, singlet, $-OC\underline{H}_3$), 7.03 and 7.72 (4H, A_2B_2 quartet, $J=8$ Hz, Ar–H), 7.39 (5H, singlet, Ar–H), 8.10—9.40 (5H, multiplet, pyridinium ring-H). Compound III was hydrolyzed in 10% aqueous perchloric acid (*ca.* 2 hr). After the reaction mixture had been worked-up as described for compound II, the residue was subjected to column chromatography on neutral alumina with acetonitrile as the eluent. The resulting yellow crystals were recrystallized from methanol to give 1-(4-aminophenyl)pyridinium perchlorate as yellow needles; mp 230°. *Anal.* Calcd for $C_{11}H_{11}ClN_2O_4$: C, 48.80; H, 4.07; N, 10.35. Found: C, 47.80; H, 4.09; N, 10.17. IR ν_{max}^{Nujol} cm^{-1}: 3500, 3400, 1630, 1510, 1100. NMR (DMSO-d_6) δ: 4.85 (2H, broad singlet, $-N\underline{H}_2$), 6.85 and 7.40 (4H, A_2B_2 quartet, $J=8$ Hz, Ar–H), 8.00—8.90 (5H, multiplet, pyridinium ring-H).

c) Ie (130 mg) was subjected to electrolysis in acetonitrile (40 ml) containing 0.1 M $NaClO_4$ and 0.4 ml of 70% perchloric acid at 1.45 V at 0° as described in a). The electrolyzed solution was concentrated to one-tenth of its original volume under reduced pressure, and then diluted with 1% aqueous sodium bicarbonate (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 silica gel with chloroform as the eluent. The crystals obtained from the first effluent were recrystallized from methanol to give pale yellow needles, which were identified as 7-methoxy-2-phenyl-1,3,4-benzoxazine-4-spiro-1′-cyclohexa-2′,5′-diene-4′-one (IVe); mp 141°. *Anal.* Calcd for $C_{20}H_{15}NO_3$: C, 75.71; H, 4.73; N, 4.42. Found: C, 75.34; H, 4.80; N, 4.46. MS *m/e*: 317 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670, 1630, 1590. UV $\lambda_{max}^{methanol}$ nm (ε): 237 (34900). NMR ($CDCl_3$) δ: 3.80 (3H, singlet, $-OC\underline{H}_3$), 6.23 and 6.82 (4H, A_2B_2-like quartet, $J=10$ Hz, ring-H), 6.60—7.00 (3H, multiplet, Ar–H), 7.30—8.20 (5H, multiplet, Ar–H). A little of the electrolyzed solution was used to estimate the yield of IVe by HPLC, and it was found to be 63%.

Two other cyclization products were obtained similarly. 5,7-Dimethoxy-2-phenyl-1,3,4-benzoxazine-4-spiro-1′-cyclohexa-2′,5′-diene-4′-one (IVf) (pale yellow needles) had mp 182°. *Anal.* Calcd for $C_{21}H_{17}NO_4$: C, 72.62; H, 4.90; N, 4.03. Found: C, 72.46; H, 4.94; N, 4.18. MS *m/e*: 347 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1670, 1630, 1590. UV $\lambda_{max}^{methanol}$ nm (ε): 237 (27300). NMR ($CDCl_3$) δ: 3.67 and 3.85 (6H, two singlet, $-OC\underline{H}_3$), 6.26 and 6.76 (4H, A_2B_2-like quartet, $J=10$ Hz, ring-H), 6.27 (1H, doublet, $J=2$ Hz, Ar–H), 6.40 (1H, doublet, $J=2$ Hz, Ar–H), 7.30—8.30 (5H, multiplet, Ar–H).

3-Phenyl-1H-naphth[1,2-*e*][1,3]oxazine-1-spiro-1′-cyclohexa-2′,5′-diene-4′-one (IVg) (pale yellow needles)

had mp 254°. *Anal.* Calcd for $C_{23}H_{15}NO_2$: C, 81.90; H, 4.45; N, 4.15. Found: C, 81.84; H, 4.48; N, 4.20. MS *m/e*: 337 (M^+). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660, 1620, 1590. UV $\lambda_{max}^{methanol}$ nm: 237. NMR ($CDCl_3$) δ: 6.41 and 7.07 (4H, A_2B_2-like quartet, $J=10$ Hz, ring-H), 7.20—8.30 (11H, multiplet, Ar–H). Another structure can be considered for this compound, that is, 2-phenyl-4H-naphth[2,3-*e*]-1,3-oxazine-4-spiro-1′-cyclohexa-2′,5′-diene-4′-one. The spectral data obtained do not rule out this possibility. However, anodic substitution and coupling of 2-naphthols have been shown to occur at the 1-position,[19] and hence the structure suggested in Chart 2 seems more likely.

References and Notes

1) M. Masui and H. Ohmori, *J. Chem. Soc. Perkin II*, **1972**, 1882.
2) S. Ikenoya, M. Masui, H. Ohmori, and H. Sayo, *J. Chem. Soc. Perkin II*, **1974**, 571.
3) P. Martinet, J. Simonet, and J. Tendil, *C. R. Acad. Sci. Paris*, **268**, 2329 (1969).
4) M. Masui and H. Ohmori, *J. Chem. Soc. Perkin II*, **1973**, 1112.
5) H. Siegerman, "Technique of Electroorganic Synthesis," ed. by N.L. Weinberg, John Wiley and Sons, Inc., New York, 1975, Part II, Appendix.
6) K. Tabei and E. Saitou, *Bull. Chem. Soc. Jpn.*, **42**, 1440 (1969); M.A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Am. Chem. Soc.*, **93**, 586, 590 (1971); J.W. Pavlik and A. van Putten, *Tetrahedron*, **27**, 3007, 3301 (1971).
7) G. Briere, R. Herino, and F. Mondon, *Mol. Cryst. Liq. Cryst.*, **19**, 157 (1972).
8) J.F. O'Donell and C.K. Mann, *J. Electroanal. Chem.*, **13**, 157 (1967).
9) The possibility of this reaction sequence had also been taken into account in the anodic pyridination of N-benzylidene-*p*-anisidines (Ref. 4), but it was discarded on the basis of the effects of 2,6-lutidine on the electrochemistry of the Schiff bases. Since 2,6-lutidine showed essentially the same effects on the electrochemistry of I as on that of the Schiff bases, if this mechanism is the case the role of 2,6-lutidine must be explained in a different way. Unfortunately, no stable product has so far been identified on electrolysis of I and the Schiff bases in acetonitrile containing 2,6-lutidine.
10) H. Lund, *Acta Chem. Scand.*, **11**, 1323 (1957); G. Manning, V.D. Parker, and R.N. Adams, *J. Am. Chem. Soc.*, **91**, 4584 (1969); V.D. Parker and L. Eberson, *Tetrahedron Lett.*, **1969**, 2843; *idem*, *Acta Chem. Scand.*, **24**, 3542 (1970); V.D. Parker, *J. Electroanal. Chem.*, **36**, 8 (1972); G.M. Blackburn and J.P. Will, *J.C.S. Chem. Commun.*, **1974**, 67.
11) J.B. Kerr, T.C. Jempty, and L.L. Miller, *J. Am. Chem. Soc.*, **101**, 7338 (1979) and references therein.
12) M. Sainsbury and J. Wyatt, *J. Chem. Soc. Perkin I*, **1979**, 108; U. Palmquist, A. Nilsson, T. Pettersson, A. Ronlan, and V.D. Parker, *J. Org. Chem.*, **44**, 196 (1979) and references therein.
13) Formation of *p*-benzoquinone and protonated starting material was detected.
14) The dication diradical can be formed in two ways. One involves intramolecular electron transfer from the aryloxy part of the molecule to the doubly charged anisidine moiety. The other involves deprotonation of the radical dication (VII) followed by further electron transfer from the aryloxy part. Both reactions seem reasonable because the oxidation potential of the aryloxy part must be similar to the second anodic peak potential of the corresponding imidate ester, as judged from the oxidation potential of related esters: E_p values in acetonitrile with and without perchloric acid (V *vs.* S.C.E.) are PhCOO-3-MeO–C_6H_4, 1.70; PhCOO-3,5-$(MeO)_2$–C_6H_3, 1.55; PhCOO-2-naphthyl, 1.65.
15) A. Ronlan, O. Hammerich, and V.D. Parker, *J. Am. Chem. Soc.*, **95**, 7132 (1973).
16) *a*) G.D. Lander, *J. Chem. Soc.*, **1902**, 591; *b*) K.B. Weiberg and B.I. Rowland, *J. Am. Chem. Soc.*, **77**, 2205 (1955).
17) P.E. Titus, P.A. Forte, and J.M. Prokipcap, *Can. J. Chem.*, **54**, 647 (1976).
18) J.F. O'Donnell, J.T. Ayres, and C.K. Mann, *Anal. Chem.*, **37**, 1161 (1965).
19) L. Papouchado, R.W. Sandford, G. Petrie, and R.N. Adams, *J. Electroanal. Chem.*, **65**, 275 (1975).