

Anodic Oxidation of Aryl-olefins

II.¹ Acetoxylation of Anisylethylenes

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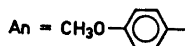
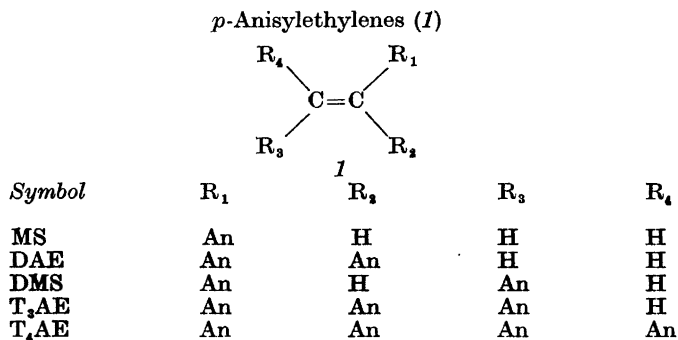
Voltammetry, coulometry, and product studies of the anodic acetoxylation of *p*-anisylethylenes show that two basic reaction pathways are followed. *p*-Methoxystyrene and 4,4'-dimethoxystilbene both undergo one electron oxidation to form a cyclized dimeric monoacetate. The more highly substituted compounds, tri-*p*-anisylethylene and tetra-*p*-anisylethylene undergo two electron oxidation to the dications. In the presence of acetate ion, tri-*p*-anisylethylene dication reacts to give the diacetate. Products resulting from a dication are also observed when anodic acetoxylation of 4,4'-dimethoxystilbene is carried out at anode potentials greater than +1.2 V. The voltammetry and product from 1,1-di-*p*-anisylethylene are anomalous. The major product isolated from the anodic acetoxylation of 1,1-di-*p*-anisylethylene does not contain acetate and results from coupling of cation-radicals at ring positions.

Although anodic substitution reactions of aromatic hydrocarbons have been studied extensively in this laboratory^{2,3} and others,⁴⁻⁵ the anodic addition of nucleophiles to olefins has only been studied in a few isolated cases. The most pertinent examples are cited here; a complete documentation can be found in the literature.⁷ Mango and Bonner⁸ investigated the anodic acetoxylation of *trans*-stilbene, and O'Connor and Pearl⁹ studied the anodic addition of pyridine to 3,4-dimethoxypropenylbenzene. Anodic acetoxylation of cyclooctatetraene produces a complex mixture of products which was shown to contain *cis*- and *trans*-bicyclo[4.2.0]octa-2,4-diene-7,8-diol diacetate, cycloheptatrienecarboxyldehyde diacetate as well as *cis*- and *trans*-7-methyl-8-acetoxybicyclo[4.2.0]octa-2,4-diene.¹⁰ Anodic pyridination of trianisylethylene results in vinylic substitution, producing trianisylethylene-monopyridinium perchlorate.¹¹ The results of a complete study of the anodic pyridination and lutidination of anisyl- and phenylethylenes will appear soon.¹²

In a preliminary communication,¹ we demonstrated the usefulness of quantitative electrochemical techniques, voltammetry and coulometry, to the

study of anodic acetoxylation of 4,4'-dimethoxystilbene. It was also pointed out that either a one-electron dimerization or a two-electron addition could be carried out selectively by proper choice of the anode potential. We now report the results of a systematic study of the reactions of the *p*-anisylsubstituted ethylenes (*I*). The structures of the *p*-anisylethylenes are summarized in Chart 1.

Chart I



RESULTS AND DISCUSSION

Voltammetry. Voltammetric curves of 1.0 mM solutions of the compounds were recorded at a rotating platinum electrode and at a stationary platinum electrode. The solvent was acetonitrile, and the supporting electrolyte was lithium perchlorate (0.1 M). All potentials reported are *versus* the aqueous saturated calomel electrode (SCE). Voltammetry was also conducted in the

Table 1. Anodic voltammetry of anisylethylenes.

Com- pound ^a	E_p^b	$E_{p(\text{pyr})}^b$	E_p^b for the correspond- ing phenyl derivative	i_p^c	$i_{p(\text{pyr})}^c$	n^d	$n_{(\text{pyr})}^d$
MS	+1.33	+1.35	+1.84	72	152	1	2
DAE	+1.60	+1.29	+1.66	256	134	4	2
DMS	+0.92	+1.00	+1.36	98	102	1	1
T ₃ AE	+0.96	+0.94	+1.42	150	160	2	2
T ₄ AE	+0.78	+0.78	+1.30	158	170	2	2

^a See Chart I.

^b Measured *vs.* SCE at a stationary platinum electrode.

^c Current recorded at a scan rate of 10 V/min.

^d Number of electrons.

same solvent-electrolyte system in the presence of pyridine (10 mM). The peak potentials of the compounds both in the presence and absence of pyridine are recorded in Table 1 along with the peak current observed at a voltage scan rate of 10 V/min. For comparison, the peak potential for the corresponding phenylsubstituted ethylene is included.

A comparison of the peak potential (E_p) for the anisylethylenes with that of the corresponding phenylethylenes reveals that in all cases except DAE, the phenylethylene is about 0.5 V more difficultly oxidized. The 1,2-disubstituted compound, DMS, is about 0.4 V more easily oxidized than the mono-anisyl compound, MS. Substitution by a third anisyl group, T_3AE , does not significantly change E_p , while the fully substituted compound, T_4AE , is oxidized 0.15 V more easily. On the basis of these results, DAE would be expected to exhibit an E_p of about the same magnitude as MS. However, DAE was observed to oxidize about 0.3 V more anodic than MS. Furthermore, DAE undergoes loss of about 4 electrons per molecule, whereas both MS and DMS undergo one electron oxidation. A more normal sequence of peak potentials is observed when the measurements are conducted on solutions 10 mM in pyridine (Table 1). DAE is still more difficultly oxidized than DMS, but only 0.3 V in this case, and is more easily oxidized than MS.

The number of electrons (n) involved in the oxidations was determined by the values of the peak currents as well as by controlled potential coulometry (see next section). MS and the symmetrically substituted compound, DMS, both undergo one electron oxidation at the stationary platinum electrode. The life-time of the intermediate cation-radical is short in both cases, since no reduction current was observed during cyclic voltammetry for either compound employing sweep rates as high as 40 V/min. The trisubstituted compound, T_3AE , undergoes a two-electron transfer to the dication which likewise

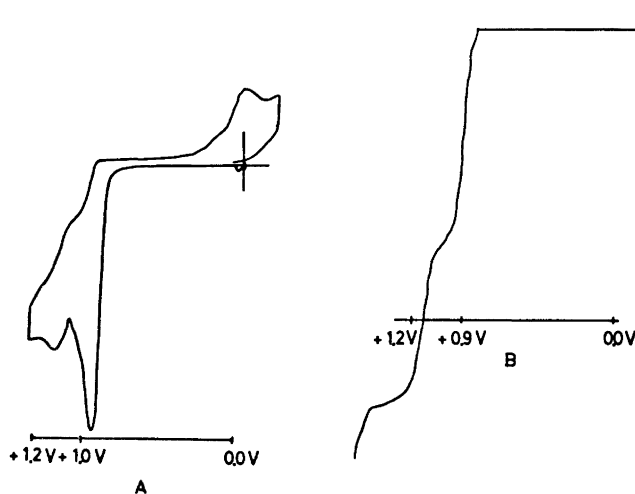


Fig. 1. Anodic voltammetry of 4,4'-dimethoxystilbene in acetonitrile. A, at a stationary platinum electrode. B, at a rotating platinum electrode.

cannot be detected by cyclic voltammetry under the conditions of this investigation. On the other hand, T₄AE, undergoes a reversible two-electron oxidation to the dication which is stable for several hours in acetonitrile.^{13,14} In the presence of pyridine, all the compounds, with the exception of DMS, give peak currents corresponding to the transfer of two electrons. A stable pyridinium salt formed during the anodic pyridination of 3,4-dimethoxypropenylbenzene has been reported.⁹

The voltammetric curves for DMS at the rotating platinum electrode and the stationary platinum electrode are illustrated in Fig. 1. At the stationary electrode, a one electron oxidation peak is observed at +0.92 V along with a small peak at +1.15 V (Fig. 1A). On the reverse scan, the only cathodic peak observed is that for reduction of the proton at +0.1 V. At the rotating platinum electrode, two oxidation waves are observed with half-wave potentials of +0.90 V and +1.15 V (Fig. 1B). In the presence of pyridine, analogous behavior is observed at both electrodes. The differences in behavior at the rotating and stationary electrodes points out the desirability of using both techniques in a voltammetric study of oxidation mechanisms. Oxidation peaks subsequent to the first at the stationary electrode are a consequence of further oxidation of the product formed at the first peak. If a change in mechanism occurs at higher potentials, for example, if the substrate oxidizes by one electron transfer at the potential of the first peak, but undergoes two electron transfer at some higher potential, this change in mechanism could go undetected if only the stationary electrode was employed, since in sweeping out to the higher potential, the substrate in the vicinity of the electrode has already undergone oxidation by the first mechanism. This is, in fact, found to be the case for DMS. Voltammetry at the stationary electrode (Fig. 1A) indicates a single one-electron oxidation at +0.92 V, while voltammetry at the rotating electrode (Fig. 1B) indicates a one-electron oxidation at +0.90 V and a second one electron transfer at +1.15 V. Without the data from the stationary electrode, it is not possible to determine whether the second wave at the rotating electrode involves further oxidation of the intermediate formed at the first wave or not. Therefore, the two techniques are complimentary and both are essential to the voltammetric study of anodic oxidation mechanisms.

Coulometry. Controlled potential coulometry was carried out on millimolar solutions of the compounds in a mixed solvent system, MeCN – HOAc (3:1) containing sodium acetate (0.25 M) and lithium perchlorate (0.1 M) as supporting electrolyte as well as in MeCN containing lithium perchlorate (0.1 M) and pyridine (10 mM). The MeCN – HOAc system has been found to be an excellent medium for studying anodic acetoxylation. The MeCN has the effect of lowering the resistance of the solution without influencing the nature of the anode processes. Sodium acetate is soluble in this system but nearly insoluble in MeCN alone. The presence of acetic acid has a further advantage in making a divided cell unnecessary due to the ready reduction of protons from the solvent. Coulometry in the presence of pyridine is particularly useful, since the products are stable pyridinium salts and integral *n* values are observed.¹⁵ The experiments summarized in Table 2 are representative of many coulometric runs conducted on these compounds.

Table 2. Coulometry for oxidation of anisylethylenes.

Run	Substrate ^a	Medium ^b	Anode potential ^c	<i>n</i> ^d
1	MS	a	+1.35	0.9
2	MS	b	+1.35	0.9
3	DAE	a	+1.50	1.0
4	DAE	b	+1.35	1.1
5	DMS	a	+0.90	1.1
6	DMS	a	+1.20	2.1
7	DMS	b	+0.90	1.0
8	DMS	b	+1.20	1.9
9	T ₃ AE	a	+1.00	2.0
10	T ₃ AE	b	+1.00	1.9
11	T ₄ AE	a	+1.00	2.0
12	T ₄ AE	b	+1.00	2.1

^a Concentration 1.0 mM.

^b a=MeCN-HOAc, NaOAc (0.25 M); b=MeCN, pyridine (10 mM).

^c V vs. SCE.

^d Determined by integration of the current-time curves.

Coulometry of MS in MeCN-HOAc in the presence of sodium acetate (0.25 M) resulted in the consumption of one Faraday per mole of substrate (Run 1). The oxidation was accompanied by film formation on the anode, and it was necessary to clean the electrode six times during the oxidation of a 1.0 mM solution. Coulometry in the presence of pyridine likewise produced an *n* value of unity. This experiment was not hampered by film formation. Both acetoxylation and pyridination of DAE could be followed coulometrically, and the passage of one Faraday per mole of substrate was observed in both cases. Film formation was also a problem in the coulometry of DAE.

Controlled potential coulometry of DMS produced the most interesting results. Acetoxylation at +0.90 V (Run 4) was accompanied by the passage of one Faraday per mole, while the same system produced an *n* value of two when the oxidation was conducted at an anode potential of +1.20 V (Run 5). Pyridination also involves either one electron (Run 6) or two electron (Run 7) coulometry depending on the anode potential.

Both T₃AE and T₄AE produced coulometric *n* values of two regardless of the anode potential employed.

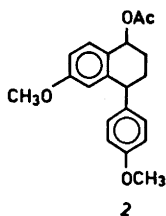
Products. For purpose of product identification, exhaustive controlled potential electrolyses were carried out in MeCN-HOAc (3:1) containing sodium acetate (0.25 M) using 1.0 mM of the substrate. Structures of the products were assigned on the basis of IR, mass, and NMR spectra (see also Experimental section).

p-Methoxystyrene (MS) undergoes one electron oxidation to form the dimerized monoacetate, 2 (Chart II). Electrode filming was so severe in this case that it was quite difficult to obtain enough product for analysis. However, the IR, NMR, and mass spectra of the oily crude product are all in accordance with the assigned structure.

Chart II

p-Methoxystyrene

Voltammetry -- 1e, irreversible oxidation
 Coulometry -- $n=1$
 Product

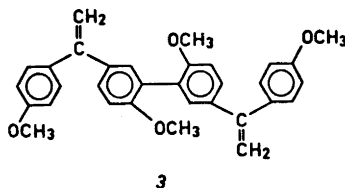


1,1-Di-*p*-anisylethylene (DAE) also undergoes one electron anodic oxidation to form a dimer (Chart III). However, the IR spectrum of the crude product failed to show the presence of an acetate group. The NMR spectrum gave a ratio of 3:1 for methoxy to vinyl protons (as is observed in the spectrum of the substrate). The highest peak in the mass spectrum was strong at $m/e = 478$, which is the parent ion of the dimer, 3. 2,5-Dimethoxytoluene has recently been shown to form the substituted biphenyl on anodic oxidation in acetonitrile¹⁶ and several other methoxybenzenes with vacant positions *ortho* to the methoxy group undergo this reaction rather than substitution in the presence of a nucleophile.¹⁷

Chart III

1,1-Dianisylethylene

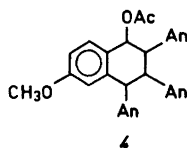
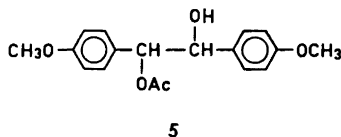
Voltammetry $>2e$, irreversible oxidation
 Coulometry $n=1$
 Product



At an anode potential of +0.90 V, 4,4'-dimethoxystilbene (DMS) undergoes one electron oxidation to form the tetralin derivative, 4 (Chart IV). At +1.20 V the major product is the hydroxy acetate, 5, and a small amount (~5%) of the meso diacetate is also obtained. At +1.1 V, a mixture of products was obtained which was estimated to consist of approximately equal amounts of 4 and 5 by NMR. The coulometry of this run was consistent with this analysis in that 1.5 Faraday per mole of substrate was consumed during the electrolysis.

Chart IV

4,4'-Dimethoxystilbene

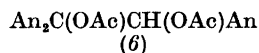
Voltammetry $n=1$ at $+0.9$ V $n=2$ at $+1.2$ VCoulometry $n=1$ at $+0.9$ V $n=2$ at $+1.2$ VProducts
at $+0.9$ Vat $+1.2$ V

Tri-*p*-anisylethylene (T_3AE) undergoes two electron oxidation in the above media to form the diacetate, **6** (Chart V), which was isolated as a white crystalline solid. The NMR spectrum of the crude product gave the proper integration of methoxy to acetate protons, indicating that the hydroxy acetate is not a significant product in this case.

Chart V

Tri-*p*-anisylethyleneVoltammetry $n=2$ Coulometry $n=2$

Product

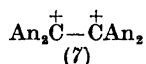


Regardless of the medium employed, tetra-*p*-anisylethylene (T_4AE) undergoes two electron anodic oxidation. In acetonitrile, the product is the stable dication^{13,14} (**7**, Chart VI). We have not been able to assign definite structures to the products obtained when the electrolysis is carried out in the presence of acetate ion. Cyclization of the dication to a phenanthrene¹⁸ accompanied by reaction with acetate ion appears to occur. The mass spectrum of the crude product shows that dimeric products are formed, probably during further oxidation of the phenanthrene.

Chart VI

Tetra-*p*-anisylethyleneVoltammetry $n=2$ Coulometry $n=2$

Product



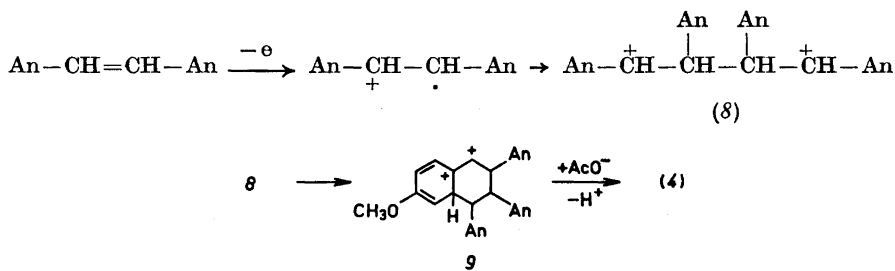
Mechanism. From the varied nature of the products observed during anodic acetoxylation of *p*-anisylethylenes, it is obvious that no single mechanism may be written to account for the reactions of all the substrates. However, a few generalizations which appear to be valid may be made.

The more highly substituted ethylenes, T₃AE and T₄AE, are oxidized by two electron transfers to the intermediate dications. The actual electron transfer may consist of consecutive one electron transfers, however, if this is the case, the oxidation potentials for the substrates and the intermediate cation-radicals are too close together to be separated by the voltammetric techniques employed. The near reversibility of the anode process involved in the oxidation of T₄AE has been discussed.¹⁴ The product of the T₃AE oxidation in the presence of acetate ion is the dication which reacts with acetate ion in a straight-forward manner to give the diacetate. Products arising from the T₄AE dication reflect the homogeneous reactivity since the dication is stable under the cyclic voltammetric conditions even in the presence of acetate ion.

When DMS is oxidized at +0.90 V, the cation radical is the initial product. This species is apparently more reactive as a radical than as a cation, since only dimerization is observed even in the presence of strong nucleophiles such as pyridine and acetate ion. The product of the dimerization must be the dication, 8,¹⁹ which undergoes cyclization to 9, rather than reactions with nucleophiles (Chart VII). These reactions must be extremely fast and could possibly occur in some concerted manner that does not involve actual formation of the intermediates, 8 and 9, as discrete species.

Chart VII

Mechanism of the cyclization reaction



DMS undergoes two electron oxidation at higher potentials with a peak potential equal to +1.15 V in acetonitrile. For all practical purposes, this may be considered a two electron transfer, however, from a kinetic viewpoint, it is possible that the cation-radical is the initial intermediate with a rate constant for dimerization (k_d) which is large compared to the rate constant for electron transfer to the dication (k_e) at low potentials. Since k_e is a function of the anode potential, and gets larger with increasing potential, a point is reached where $k_e' \gg k_d$ and only products resulting from the dication are observed. Since we cannot distinguish between direct two-electron and conse-

cutive one-electron transfers in this case, we will consider this a two-electron oxidation without specifying the detailed mechanism.²⁰

The anodic oxidation of 1,1-dianisylethylene (DAE) produces a cation-radical which apparently has higher spin density on the aromatic nuclei than on the positions of the olefinic linkage, since the dimer (biphenyl type) is the only observed product. The voltammetry, coulometry, and product from this substrate appear to be anomalous and warrant further investigation.

The anodic acetoxylation of *p*-methoxystyrene (MS) parallels that of the one-electron oxidation of DMS with the substituted tetralin being the only detected product. No change in the product could be detected by conducting the oxidation at higher anode potentials.

Table 3. NMR and mass spectral data of products.

Substrate	Product	NMR δ (ppm)			<i>m/e</i> (relative abundance, %)
		CH ₃ O—	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{C}-\text{O}- \end{array}$	=CH ₂	
MS	2	3.75(6H)	2.06(3H)		326 (8.6), 282 (12), 266 (100), 251 (18), 235 (5)
DAE	3	3.76(6H)		5.23(2H)	478 (100), 359 (66), 242 (48), 240 (40), 227 (29)
DMS	4	3.70(9H)	2.20(3H)		538 (4.6), 479 (100), 358 (98), 297 (1.8)
DMS	Diacetate from 5	3.75(3H)	1.95(3H)		358 (45), 298 (27.5), 257 (42.5), 256 (42.5), 240 (100), 239 (50)
T ₃ AE	6	3.75 3.78(9H) 3.81	1.90(3H) 1.96(3H)		464 (trace), 405 (15), 362 (39), 346 (100)

EXPERIMENTAL

Reagents. *p*-Methoxystyrene, 4,4'-dimethoxystilbene, and the supporting electrolyte, lithium perchlorate, were reagent grade and used without further purification. 1,1-Dianisylethylene was prepared by the reaction of di-*p*-anisylketone with methylmagnesium iodide followed by heating in 85 % phosphoric acid.²¹ Tri-*p*-anisylethylene²¹ and tetra-*p*-anisylethylene¹³ were prepared by published procedures. Acetonitrile was purified by two distillations from phosphorus pentoxide in which only the middle 60 % fraction was collected. Acetic acid was purified by crystallization.

Voltammetry. Both single sweep (at a rotating platinum electrode), and cyclic voltammetry (at a Beckman platinum button electrode No. 39273) were carried out with a Heath EUW 198 operational amplifier with polarography module EUA-19-2. All potentials are expressed in volts relative to the aqueous saturated calomel electrode (SCE).

Coulometry. Controlled potential coulometry was conducted on 1.0 mM solutions. Coulometric *n* values were determined by integration of the current-time curves. The potential of the working electrode was controlled by an Amel (Model 555) potentiostat. The anode was a platinum gauze electrode, and the cathode a carbon rod. When acetic acid was present in the solvent system, no cell divider was used. A glass frit was used to separate anode and cathode compartments for the coulometric pyridination experiments.

Preparative electrolyses. The preparative experiments were conducted in the same apparatus as used for coulometry. Substrate (1.0 mol, 20.0 mM solution) was exhaustively oxidized until the current dropped to residual levels. The electrolysis mixture was poured into a separatory funnel containing chloroform (100 ml). The chloroform phase was extracted with several equi-volume portions of water. After drying over anhydrous magnesium sulfate, the chloroform was removed under the aspirator. In order to avoid fractionation of products, the crude product was analyzed directly by IR, NMR, and mass spectrometry. Analysis after further purification indicated that the crude product contained only one major component in all cases.

The structure of the hydroxyacetate (5) from DMS was established by conversion to the diacetate and comparing IR, mass, and NMR spectra with that of the authentic compound. Structures were assigned to the other products on the basis of the IR, mass, and NMR spectra. NMR and mass spectral data of the products are summarized in Table 3.

REFERENCES

1. Part I. Parker, V. D. and Ebersson, L. *Chem. Commun.* **1969** 340.
2. Ebersson, L. *J. Am. Chem. Soc.* **89** (1967) 4669.
3. Ebersson, L. and Nyberg, K. *J. Am. Chem. Soc.* **88** (1966) 1686; *Acta Chem. Scand.* **18** (1964) 1567.
4. Parker, V. D. and Burgert, B. E. *Tetrahedron Letters* **1965** 4065; **1968** 2415.
5. Parker, V. D. *Chem. Commun.* **1968** 1164.
6. Ross, S. D., Finkelstein, M. and Petersen, R. C. *J. Am. Chem. Soc.* **86** (1964) 4139.
7. For a recent review, see Weinberg, N. L. and Weinberg, H. R. *Chem. Rev.* **68** (1968) 449.
8. Mango, F. D. and Bonner, W. A. *J. Org. Chem.* **29** (1964) 1367.
9. O'Connor, J. J. and Pearl, I. A. *J. Electrochem. Soc.* **111** (1964) 335.
10. Ebersson, L., Nyberg, K., Finkelstein, M., Petersen, R. C., Ross, S. D. and Uebel, J. J. *J. Org. Chem.* **32** (1967) 16.
11. Parker, V. D. and Ebersson, L. *Chem. Commun.* **1969** 451.
12. Parker, V. D. and Ebersson, L. *Unpublished work.*
13. The dication of T₄AE formed by chemical oxidation was first reported by Buckles and coworkers; Baenziger, N. C., Buckles, R. E. and Simpson, T. D. *J. Am. Chem. Soc.* **89** (1967) 3405; Buckles, R. E. and Wormer, W. D. *J. Am. Chem. Soc.* **80** (1958) 5055.
14. Parker, V. D., Nyberg, K. and Ebersson, L. *J. Electroanal. Chem.* **22** (1969) 150.
15. Lund, H. *Acta Chem. Scand.* **11** (1957) 1323.
16. Parker, V. D. and Adams, R. N. *Tetrahedron Letters* **1969** 1721.
17. Parker, V. D. and Adams, R. N. *Unpublished results.*
18. Phenanthrenes have been reported to form on anodic oxidation of tetraphenyl- and tetra-*p*-anisylethylene in acetonitrile; Ohnesorge, W. E. *Extended Abstracts, Electrochemical Society Meeting, New York 1969.*
19. Dications of this type have been postulated as products during dimerization of 1,1-bis-(*p*-dimethylaminophenyl)ethylene; Bawn, C. E. H., Bell, F. A. and Ledwith, A. *Chem. Commun.* **1968** 599.
20. A similar case, where either an EC or EEC mechanism occurs depending only on the anode potential has been observed during anodic acetoxylation of 9,10-dimethylanthracene; Parker, V. D. *Chem. Commun.* **1969** 848.
21. Shelton, R. S., Van Campen, M. G., Jr., Meisner, D. F., Parmarter, S. M., Andrews, E. R., Allen, R. E. and Wyckoff, K. K. *J. Am. Chem. Soc.* **75** (1953) 5491.

Received April 25, 1970.