

A Tripositive Organic Ion: Anodic Pyridination of Tris-*p*-methoxyphenylethylene

By VERNON D. PARKER and LENNART EBERSON*

(Division of Organic Chemistry, University of Lund, Chemical Center, P.O. Box 740, S-22007, Lund, Sweden)

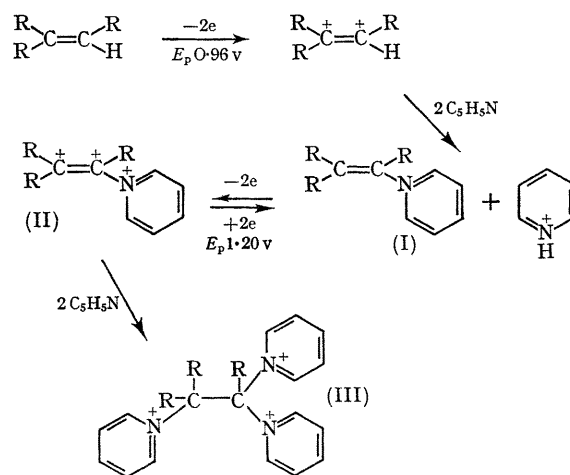
Summary Anodic oxidation of tris-(*p*-methoxyphenyl)-ethylene in the presence of pyridine results in the intermediate formation of the monopyridinium salt of a trication, which undergoes quasi-reversible reduction under cyclic voltammetry conditions.

We report the generation of a trication during the anodic pyridination of tris-(*p*-methoxyphenyl)ethylene. The reaction occurs by two successive 2e-oxidations involving the pyridinium intermediate, (I) (Scheme).

Tris-*p*-methoxyphenylethylene (T₃ME) undergoes an irreversible 2e-oxidation at a platinum anode in acetonitrile. That the life-time of the dication is short is indicated by the failure to observe any reduction current for the dication during cyclic voltammetry at moderately rapid sweep rates (up to 40 v/min.). This behaviour is in direct contrast with that of tetrakis-(*p*-methoxyphenyl)ethylene (T₄ME) which undergoes a reversible 2e-oxidation to the dication which is stable in acetonitrile (Figure 1A).^{1,2} The oxidation peak, O₁, involves the transfer of 2e, as shown by controlled-potential coulometry. No cathodic current is observed on reversing the direction of the scan. Cyclic voltammetry in the presence of pyridine (10 mM) is illustrated in Figure 1B. In this case, two successive 2e-oxidation peaks are observed, O₁ at +0.94 v (*vs.* SCE) and O₂ at +1.27 v (SCE). Some reversibility of O₂ is indicated by a small reduction peak, R₂, on scan reversal.

Controlled potential coulometry of T₃ME in the presence

of pyridine was characterised by integral values of *n*, indicating the absence of complications due to side reactions (Table).



SCHEME. R = *p*-MeO·C₆H₄-

Anodic addition of nucleophiles to the double bond of an arylolefin produces a product substantially more difficult to oxidize than the substrate.³ Thus, pyridination or acetoxylation of 4,4'-dimethoxystilbene which undergoes

oxidation at +0.92 v (*vs.* SCE), produces products which are not oxidized at potentials lower than +1.60 v. The cyclic polarogram of a 1 mM solution of T₃ME in acetonitrile after exhaustive electrolysis at +1.0 v shows a peak current

Controlled potential coulometry for the oxidation of T₃ME

Run ^a	Anode potential (v <i>vs.</i> SCE)	[Pyridine], mM	<i>n</i>	Product
1	+1.00	0	2	
2	+1.00	2	2	(I)
3	+1.00	10	2	(I)
3a ^b	+1.30	10	2	(III)
4	+1.30	10	4	(III)

^a Conducted in acetonitrile–lithium perchlorate (0.1M).

^b The same solution that had previously been oxidized at +1.0 v (run 3).

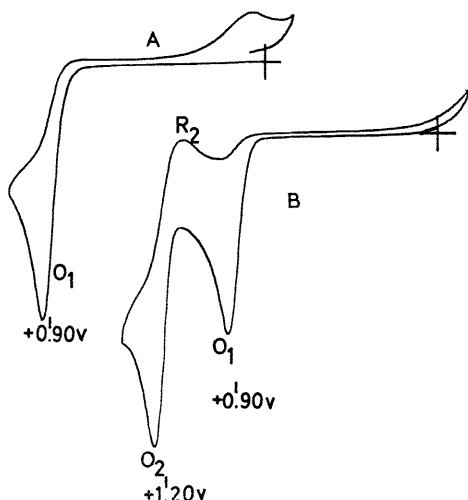


FIGURE 1. Cyclic polarogram in acetonitrile–lithium perchlorate (0.1M) for anodic oxidation of T₃ME: A. In the absence of pyridine; B. in the presence of 10 mM pyridine. Sweep rate 10 v/min.

† Continuous cycling between +0.6 and +1.4 v shows that the process involved at R₂ is regeneration of (I).

¹ V. D. Parker, K. Nyberg, and L. Ebersson, *J. Electroanalyt. Chem.*, in the press.

² The dication has been characterized; N. C. Baenziger, R. E. Buckles, and T. D. Simpson, *J. Amer. Chem. Soc.*, 1967, 89, 3405.

³ V. D. Parker and L. Ebersson, *Chem. Comm.*, in the press.

at +1.27 v nearly exactly the same as that at +0.94 v of the solution before electrolysis (Figure 1B). The voltammogram of the product (run 2) after isolation, recorded in the absence of pyridine is shown in Figure 2. The oxidation

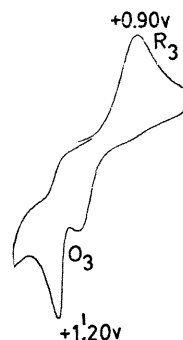


FIGURE 2. Cyclic polarogram for anodic oxidation of the mono-pyridinium salt [perchlorate of (I)]. Sweep rate 10 v/min.

peak consists of two 1e-transfers very close together: on reversal a reduction peak, R₂, corresponding to the reduction of an intermediate formed during the oxidation is observed at +0.90 v (SCE).† Addition of pyridine causes the two 1e-peaks to coalesce into a single 2e-peak and completely eliminates the reduction current.

A possible explanation is that the oxidation of (I) in the absence of pyridine is quasi-reversible to the trication, (II), which reacts rapidly in the presence of pyridine to form the tripyridinium ion, (III). The structure (I) was established on the basis of the n.m.r. spectrum and elemental analysis of the product isolated from run 2. Attempts to isolate the tripyridinium salt (III) failed. This is not surprising in view of the known instability of hexa-arylethanes.

We thank the Swedish Natural Science Research Foundation for financial support.

(Received, February 27th, 1969; Com. 281.)