

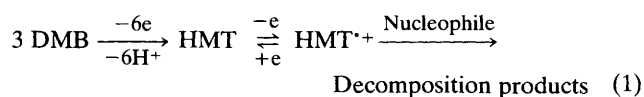
## Anodic Trimerization: a Facile One-step Synthesis of Tris(15-crown-5)triphenylene

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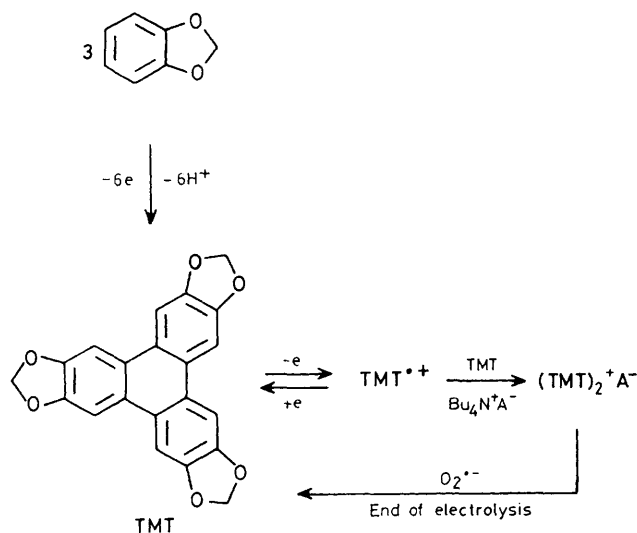
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Under unusual non-nucleophilic conditions, aromatic *ortho*-diethers undergo a remarkable cyclic trimerization leading to hexasubstituted triphenylenes; in particular, the electrochemical synthesis of a new threefold ionophore is described.

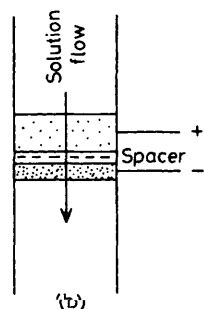
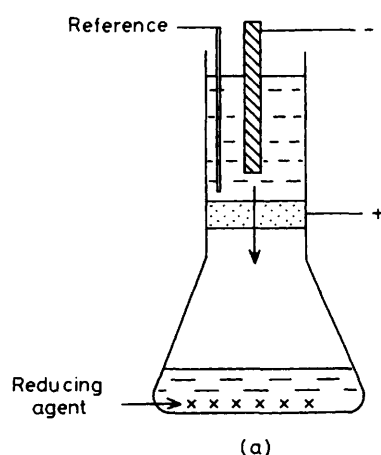
The cyclic anodic trimerization of aromatic systems has so far only concerned aromatic rings *ortho*-disubstituted by electron-donating substituents which are not involved in the oxidation process. A typical example of this was described at the beginning of the seventies by Bechgaard and Parker<sup>1</sup> when oxidizing 1,2-dimethoxybenzene (DMB) into hexamethoxytriphenylene (HMT) under rather drastic conditions (methylene chloride added with trifluoroacetic acid in order to diminish the nucleophilicity of water present as an impurity in the electrolyte), equation (1).



The difficulty of obtaining HMT was increased by the fact that HMT oxidation occurs at less positive potentials than that necessary to carry out the trimerization process. The formation in solution of HMT<sup>•+</sup> supposes fairly good stability for this transient species in order for it to be reduced back to HMT

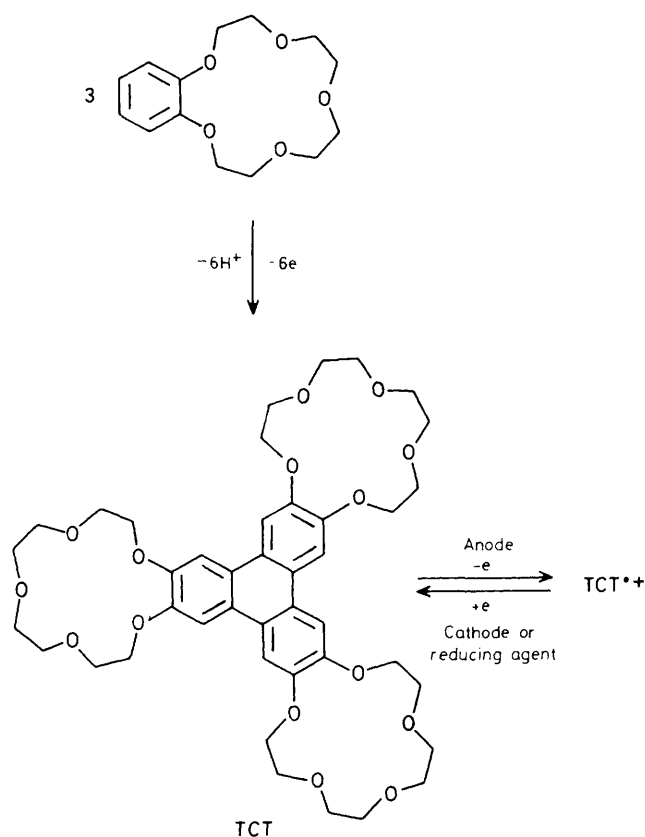


Scheme 1



**Figure 1.** Flow cells: (a) a single porous electrode cell; (b) a two porous electrode system.

at the end of the electrolysis. On the other hand, different experimental conditions<sup>2</sup> have allowed the electrocrystallization of the mixed valence salt ( $\text{HMT}_2^+ \text{A}^-$ ) ( $\text{A}^-$ : anion of the electrolyte directly from DMB). Very recently, the occurrence of the trimerization process has also been used to advantage in the formation of poly(dibenzo-crown-ethers).<sup>3</sup>



Scheme 2

The present communication aims to report the mode of formation of complex cyclic ethers from monomers possessing the structure of a polyoxamacroligand. A simple process has already been shown to involve an insoluble mixed valence salt crystallizing at the macroanode interface which can then be reduced at the end of the electrolysis by means of any efficient reducing agent: the electrogenerated superoxide anion ( $\text{O}_2^{\bullet -}$ ) was chosen in the first reported synthesis<sup>4</sup> of tris(methylenedioxy)triphenylene (TMT), which is summarized in Scheme 1.

An alternative to the process shown in Scheme 1 is now proposed, which appears to be more general and should be applicable to all soluble trimers when formed at room temperature. We describe here the use of a flow cell either with one porous anode (the anolyte solution is then chemically reduced) [Figure 1(a)] or with two porous electrodes (the anolyte is then reduced at a fast rate through a juxtaposed porous cathode) [Figure 1(b)]. Some other examples of coupling reactions using flow cells of this type have already been described when using non-aqueous solvents.<sup>5</sup> In the case of cyclic ethers, such a process allows the easy synthesis of a new triphenylene, namely tris(15-crown-5)triphenylene (TCT) with three identical cryptand sites (Scheme 2).

The experimental conditions are as follows. The porous working anodes (diameter: 40 mm) are made either of graphite felts or of platinum gauze. When only a single porous electrode is used, the reducing agent is zinc powder. The electrolyses can be carried out both in acetonitrile or in a mixture of trifluoroacetic acid and methylene chloride. They can be conducted at a constant current or at a fixed potential [ $\sim 1.1$  V vs. standard calomel electrode (s.c.e.)]. In both cases, the flow rate is adjusted assuming that the electrochemical

conversion at the electrodes is almost complete.<sup>†</sup> The mass of monomer treated in this way is of the order of 0.5–1 g. Whatever the process, the yield averages 30% of trimer (the rest being essentially unreacted starting product). TCT (recrystallized from ethanol and then acetonitrile) (m.p. = 285 °C) was characterized by various classical methods.<sup>‡</sup>

This new method is of interest owing to its mild conditions which allow the synthesis of such trimers for the first time. However fragile the polyoxa chains, the short life of the radical cations involved in the process may be able to overcome the decomposition tendency which is observed with

common inorganic oxidizers and this method therefore has potential applicability to other kinds of monomers.

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<sup>†</sup> For example, during an intensiostatic electrolysis on 250 cm<sup>3</sup> of a B15C5 solution (10<sup>-3</sup> M) and an average flow rate of 1 cm<sup>3</sup> min<sup>-1</sup>, the anodic current has to be fixed at 113 mA.

<sup>‡</sup> Mass spectroscopy (*m/z* 798, *M*<sup>+</sup>, 100%); <sup>1</sup>H n.m.r. (δ, Me<sub>4</sub>Si): 8 (6 aromatic H, s), 3.7–4.4 (48 aliphatic H, m); <sup>13</sup>C n.m.r. (δ, Me<sub>4</sub>Si): 148.6 (6 aromatic C, s), 123.0 (6 aromatic C, s), 107.3 (6 aromatic C, s), 70 (24 aliphatic C, 3s); i.r. (in KBr): 2900, 1615, 1510, 1435, 1360, 1210, 1180, 1130, 1060, 1015, 980, 940, 850, and 790 cm<sup>-1</sup>.

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