



Anodic oxidation of a tetrasubstituted cyclooctatetraene. Multiple carbon–carbon bond cleavage and aromatization

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ABSTRACT

Anodic oxidation of 1,2-,5,6-bis(trimethylene)cyclooctatetraene in methanol affords as the major product a substance formed by a complex sequence of carbon–carbon bond cleavages and concomitant aromatization.

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It is well known that cyclooctatetraene (COT, **1**) is tub-shaped but that the product of addition of two electrons by reaction with an active metal such as Na or K affords a planar dianion.^{1–4} The reason for this is obvious: the addition of two electrons converts **1** into a Hückel $4n+2$ dianion whose aromatic character requires planarity to achieve maximum *p*-orbital overlap. Such experiments, however, are not well suited for probing into the details of the reduction process, such as whether a discrete monoanion intermediate is produced or at what point in the reduction the change from the tub-shaped geometry of **1** to the planar dianion takes place. Electrochemical methods, which can characterize the nature of individual electron transfers with a fine degree of discrimination, are well suited for answering such questions. The electrochemical reduction of COT has in fact been the subject of a substantial number of studies.^{5–10} As a result of these studies, we now know, for example, that formation of the dianion takes place via two distinct one-electron transfers via an intermediate planar anion radical. (We know this from electrode kinetic studies that show that the first electron transfer is slow because of the concomitant geometry change from tub to plane and, correspondingly, that the second transfer is fast because no geometry change is required.)

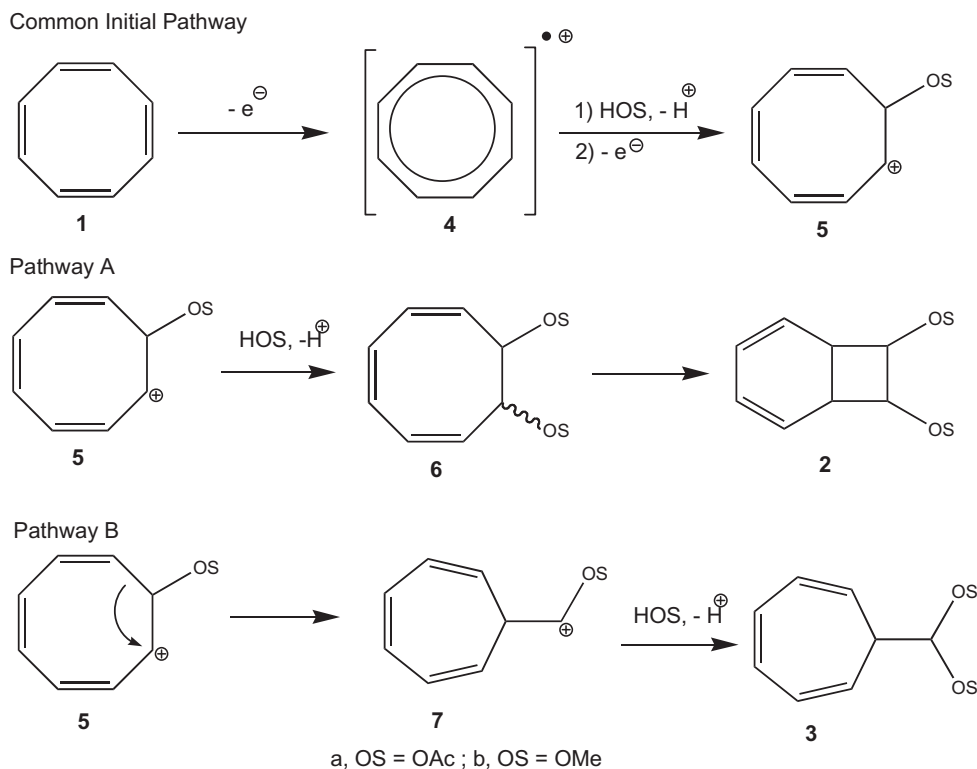
One might have expected a correspondingly substantial literature on the electrochemical oxidation of COT. But surprisingly, until recently the only report of any kind in this area was that of Ebersson, et al.¹¹ They studied the preparative scale electrochemical oxidation of **1** in acetic acid containing sodium acetate.

They found two products in a ratio of 70:30, a bicyclic diacetate (**2a**) (as a mixture of stereoisomers) and the tropyliene acylal **3a** (Scheme 1), neither of which retains the original eight-membered ring. We recently re-examined the anodic oxidation of **1**, but in methanol solvent instead of acetic acid.¹² We found that in this solvent the reaction produces only the acetal **3b**. In order to explain both the formation of two types of product produced in this electrolysis and the solvent dependence, we proposed that products **2** and **3** could be explained by a single mechanism (Scheme 1) in which the initial electron transfer affords the COT cation radical (**4**). Nucleophilic attack on **4** by solvent, followed by removal of a second electron, would afford the heptatrienyl cation **5**, which can either (a) suffer a second nucleophilic attack by solvent, leading ultimately to **2** after electrocyclic ring closure (path A) or (b) undergo a 1,2-shift to form cation **7** and final reaction with solvent to produce **3**. Quantum chemical computations were carried out, with *S* = Ac and Me on **2** and **3** and intermediates **5–7** and the transition states between **5** and **7**. The computations showed that **3** should be the thermodynamic product independent of whether the solvent is HOAc or MeOH, but that the competition between paths A and B is kinetically controlled: the activation barrier for the conversion of **5a** to **7a** is significantly higher than for **5b** to **7b**.¹² High level computations¹³ and experiment¹⁴ agree that in general 7,8-disubstituted-1,3,5-cyclooctatrienes cyclize rapidly and irreversibly to 7,8-disubstituted-bicyclo[4.2.0]-octadienes.

The conversion of **1** to **2** and/or **3** converts the COT ring, with its eight equivalent carbon atoms, into products in which a number of the carbon atoms are differently functionalized, which could be of synthetic utility. Because of their greater structural

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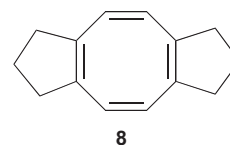
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Scheme 1. Mechanism of anodic oxidation of cyclooctatetraene in hydroxylic solvents.

complexity, we regard substances **2** as more attractive targets than **3**. However, further development of this chemistry will require that it be carried out on cyclooctatetraenes (of which many are known)^{15,16} of lower symmetry than **1**. As the first step in a planned study along these lines, we chose to study the anodic oxidation of the tricyclic COT derivative **8**, which can be prepared

by the nickel-catalyzed cycloisomerization of two molecules of 1,6-heptadiyne.¹⁷



In a preliminary cyclic voltammetry investigation, **8** was found to exhibit a well-defined irreversible wave at +0.70 V and a smaller broad wave around +0.9 V relative to Ag/AgNO₃ reference in acetonitrile containing 0.1 M LiClO₄ at a carbon working electrode (Fig. 1). A preparative scale electrolysis was carried out at +0.8 V in 90:10 acetonitrile/methanol containing tetrabutylammonium hexafluorophosphate in a divided cell using a reticulated vitreous carbon anode. Evaporation, redissolution in methanol, and chilling permitted separation of the supporting electrolyte, after which the

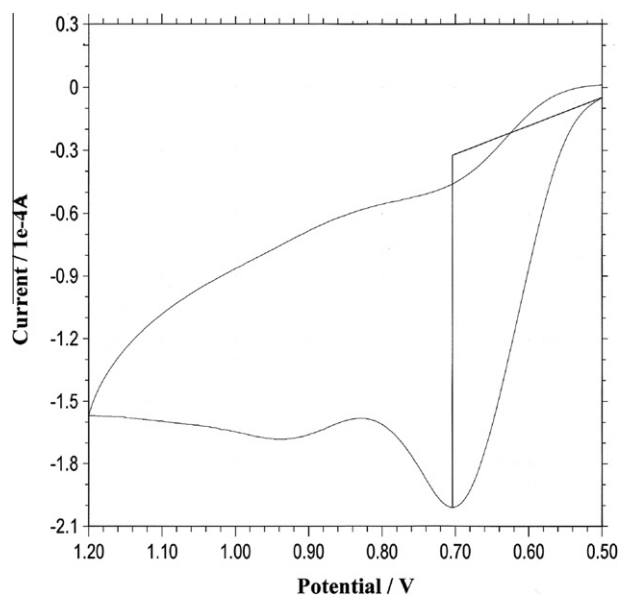


Figure 1. Cyclic voltammogram of **8** in an 0.1 M solution of lithium perchlorate in acetonitrile versus 0.1 Ag/AgNO₃ reference electrode, at a carbon rod working electrode, with platinum wire counter electrode, and a silver nitrate reference electrode. The voltammogram exhibits two oxidation peaks with the first at 0.70 V and the second between 0.9 and 1.0 V.

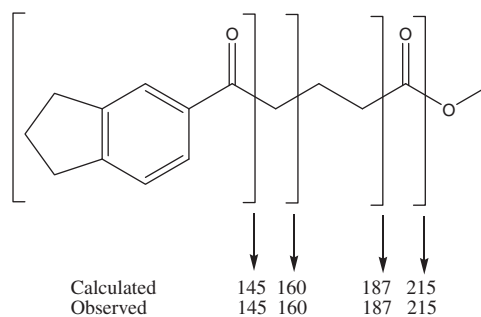


Figure 2. Major mass spectrometric fragmentation sites of **9**.

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