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REVERSIBLE ELECTROCHEMICAL OXIDATION OF 2,5,8,11-TETRA-*tert*-BUTYL-*peri*-XANTHENOXANTHENE TO ITS RADICAL CATION AND DICATION

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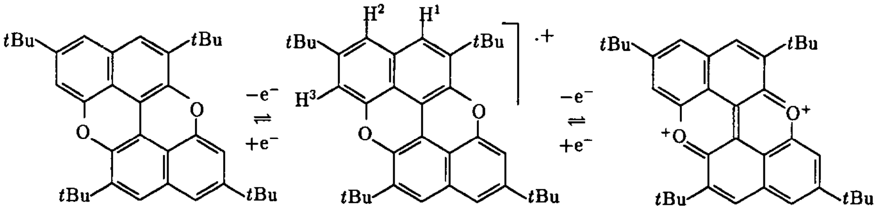
Summary – The electrochemical oxidation of tetra-*tert*-butyl-*peri*-xanthenoxanthene **1** to its dication **3** *via* the corresponding radical cation **2** is investigated. The electrochemical properties of **2** and **3** and the ESR spectrum of **2** are discussed. A product of the reaction of **3** with water is described.

The increasing interest in the chemistry of organic dications as compared to the corresponding radical cations has recently been pointed out by Parker and Tilset[1]. In this regard, the analysis of a system where both "oxidation states" are persistent on the time-scale of voltammetry may open the opportunity to determine the formal potentials of the two redox couples. The shorter life-time of both cationic species in the presence of nucleophiles on the other hand should still allow for an examination of their chemical reactivity. In this context, we have investigated the formation of the dication **3** derived from 2,5,8,11-tetra-*tert*-butyl-*peri*-xanthenoxanthene **1**[2,3], which is isoelectronic to a substituted anthanthrene **4**[4]. Both, dication **3** and hydrocarbon **4**, possess a 22 π-electron system which is expected to be relatively stable. Furthermore, **1** also may be a good donor for charge transfer interactions with acceptor molecules.



1 **2** **3**

Cyclic voltammograms of **1** in CH_2Cl_2 (distilled twice over P_2O_5 and passed over a column of neutral alumina immediately before use) with tetra-*n*-butyl-hexafluorophosphate as supporting electrolyte at a Pt disc electrode show two distinct oxidation waves (Figure 1; peaks I, II, III, and IV). A detailed analysis of curves taken at various values of the scan rate v ($0.005\ V/s \leq v \leq 0.2\ V/s$) and the concentration c^0 of **1** ($10^{-4} \leq c^0 \leq 10^{-3}$ M) revealed the reversible behavior of both electron transfers: peak potentials E_p and values of $i_p/\sqrt{v} \times c^0$ are independent of v and c^0, the peak potential differences are close to 58 mV and the peak current ratios – as calculated by Nicholson's formula[5] – are unity. For both waves, Malachesky's equation[6] gave n-values around 1. The formal potentials were determined to be $E_1^0 = 0.390 \pm 0.004$ V and $E_2^0 = 1.056 \pm 0.012$ V. No indication of follow-up reactions could be detected.

We coulometrically oxidized **1** in a three compartment cell at $E = 0.5$ V. From the charge passed, $n = 0.96$ can be calculated. The resulting purple solution ($\lambda_{max} = 302, 368, 534, 712, 835$ nm) was reduced at $E = 0$ V. A charge corresponding to $n = 0.92$ was passed, additionally suggesting the reversibility of the one-electron oxidation of **1** even on the time scale of coulometry (taking into account some loss of **2** through the diaphragm due to migration).

The same purple species can be prepared by chemical oxidation of **1** with $AgClO_4/I_2$ [7]. It showed reversible reduction and oxidation waves at the same formal potentials as those observed for the oxidation of **1** in two steps. Thus, this compound is identical to the one obtained by electrochemical oxidation of **1** at $E = 0.5$ V. The purple product co-precipitated during the chemical oxidation with AgI and could not be separated from this salt without decomposition. The products of both chemical and electrochemical oxidations showed an identical ESR signal ($g = 2.00462$) with 21 lines. By comparison to simulated spectra we determined three hyperfine coupling constants ($a_{H^1} = 0.16$ mT, $a_{H^2} =$

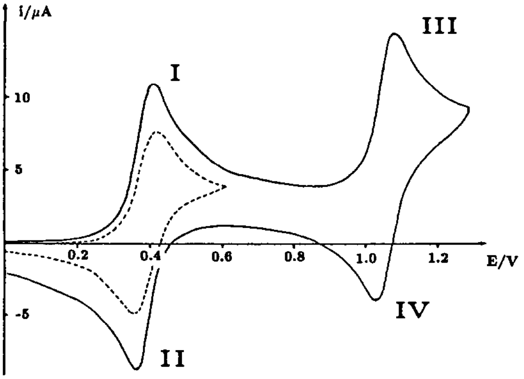
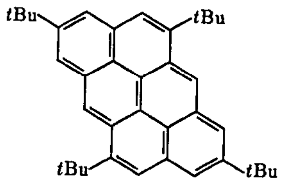


Figure 1: Cyclic voltammograms of **1** in CH_2Cl_2 with $E_\lambda = 0.6$ V (— — —; v=0.02 V/s) and 1.3 V(________; v=0.05 V/s).
Potentials are reported *vs.* the Ag/0.01 M Ag^+ reference electrode.



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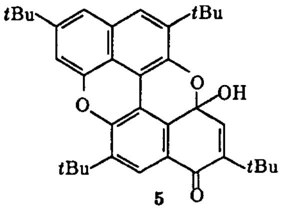

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0.325 mT, $a_{H3} = 0.27$ mT). The assignment followed the results from anisole cation radical: the proton *para* to the oxygen atom shows the highest hfs constant, protons *meta* to the oxygen atom the smallest one[8]. Thus, the product of the first oxidation step of **1** at $E = 0.5$ V was identified as the corresponding radical cation **2**. Solutions of **2** proved to be quite persistent against nucleophiles. Only after the addition of an excess of MeOH slow decolorization was observed to a yellow solution which showed a blue fluorescence typical of **1**.

Chemical oxidation of **1** in trichloroethene with an excess of $SbCl_5$ as the oxidant yielded blue solutions (λ_{max} = 640 nm) which decomposed before cyclic voltammograms could be recorded. *In situ* preparation of the corresponding oxidation product in the electrochemical cell and subsequent voltammetry was prohibited by the large background currents due to $SbCl_5$. The UV spectrum of the solution slowly changed to that of the radical cation **2** during 20 min.

Electrochemical oxidation of **1** at $E = +\ 1.25$ V on a preparative scale at 25 °C revealed that more than 2 electrons were consumed. The resulting solution was evaporated and the residue extracted with petroleum ether. Work-up of the organic phase using column chromatography yielded a red compound of m.p. 180 °C (decomposition) in 71% yield. MS and elementary analysis show that **1** has added two oxygen atoms (M^+ = 538 e/m). The IR spectrum indicates the presence of an alcoholic hydroxy group (broad OH-absorption at 3410 cm^{-1}). The ^1H NMR spectrum reveals separated signals for all 4 *tert*-butyl groups and a singlet at 3.26 ppm (OH) which disappears in the presence of D_2O. In the ^{13}C NMR spectrum absorptions at δ = 183.4 and 89.9 ppm clearly indicate the presence of a *para*-quinolide carbonyl[9] and a ketal group, suggesting structure **5**. This compound may be derived from **3** *via* addition of water (present in the solvent) in position 3 followed by deprotonation. The resulting phenol may further be oxidized at the applied potential to the corresponding phenoxenium ion[10]. Addition of a second molecule of water to this cation in position 12a and deprotonation may yield **5**, a quinone semiacetal related to the semiacetal of α-tocopherol quinone[11]. The isolation of **5**, as a result, shows the dication **3** to be the most likely intermediate in the oxidation of **1** at 1.25 V.

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