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Generation of Aryltropylium Ions by Photoinduced and Thermal Electron Transfer

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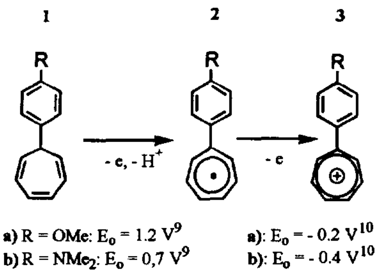
Abstract: The two step oxidation of colourless arylcycloheptatrienes to the corresponding coloured aryltropylium salts occurs either via the initiation by photoexcited electron acceptors or thermally by tetracyanoquinodimethane (TCNQ). In each case not a hydride ion is transferred but the oxidation follows the electron - proton- electron sequence

Arylcycloheptatrienes are well known to be readily converted to tropylium ions by hydride transfer to a less stable carbocation.[1] Substituted aryltropylium ions exhibit interesting properties which may favour them as anchors for temporary binding of various compounds in the binding sites of macrocycles. Depending on the donor properties of the aryl residue, the formed tropylium ions are more or less strong electron acceptors capable of binding electron donors by charge transfer interaction.[2] Amides can temporarily be bound by covalent bonds.[3] Furthermore, the colour of the tropylium ions is strongly dependent on the donor capability of the aryl substituent[4] and tropylium ions are good cations for forming highly conductive $TCNQ^{-}$ salts.[5] Cycloheptatrienes, which are precursors for tropylium cations, have been incorporated in macrocyclic arrays such as crown ethers to provide pH responsive centres.[6]

Because of the remarkable properties of tropylium ions it would be interesting to generate tropylium salts photochemically in order to switch binding properties of macrocycles containing arylcycloheptatriene units in response to light.

Whereas the formation of substituted aryltropylium ions by thermal oxidation reactions is known for a long time, there is only one report about a photoinitiated generation of tropylium ions which is associated with the photolysis of tetrabromomethane yielding tropylium cations in low chemical yields sufficient for information recording.[7]

Here, we report the photooxydation of **1** by more suitable photoexcited electron acceptors. According to the one-electron oxidation potential of **1** (Scheme 1) even weak photoexcited electron acceptors yield large negative values of the Gibbs energy change of electron transfer if there are sufficiently high energies (E_{00}) of the first excited state: $\Delta G^{o}_{et} = E^{o}_{ox} - E^{o}_{red} - E_{00} - C$ (E - redox potentials, C - Coulomb term).[8]

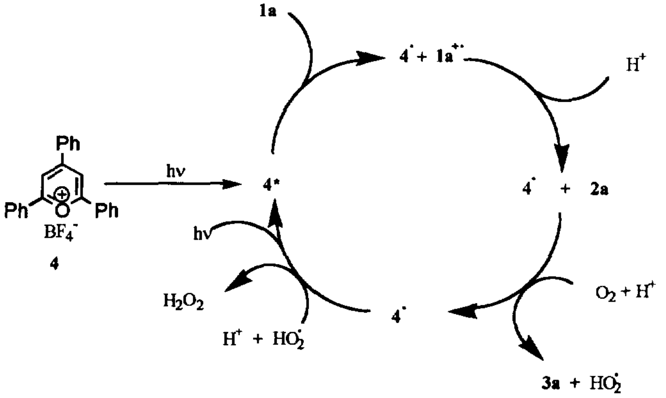


Scheme 1

A fast deprotonation of the radical cation can be assumed following the electron transfer. This is supported by the irreversible peaks measured with cycloheptatrienes by cyclic voltammetry.[9] The tropyl radical **2** has to transfer the second electron to a suitable acceptor. A second photoinduced electron transfer seems to be rather unlikely. Therefore, the used electron acceptor should be able to oxidize the tropyl radical in a thermal step. That means the reduction potential should be > - 0.2 V. Moreover, the last oxidation step must be fast. It has to compete with the combination of two tropyl radicals forming substituted bitropyl, the rate constant of which amounts to about 10^6 l/mol s.[10]

Arylsubstituted cycloheptatrienes **1a** and **1b** and two types of electron acceptors **4** and **5**, respectively, were chosen to study the photooxidation in acetonitrile solution.

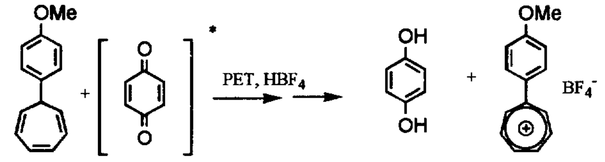
Photoexcited triphenylpyrylium tetrafluoroborate **4** oxidizes **1a** only in the presence of acids and oxygen (Scheme 2). The fluorescence of **4** is quenched efficiently by **1a** at diffusion controlled rate. Electron transfer should occur because energy transfer from excited **4** to **1a** would be an uphill process. Since **4** cannot oxidize the tropyl radical **2a** (ΔG: + 0.2 eV), oxygen in the presence of acids is necessary in order to complete the oxidation process (Scheme 2). According to the proposed mechanism the formation of H_2O_2 was proven. **4** is regenerated during the reaction. Thus, it acts as an efficient photocatalyst in the photooxidation of arylcycloheptatrienes with dioxygen. The overall quantum yield at a high concentration



Scheme 2

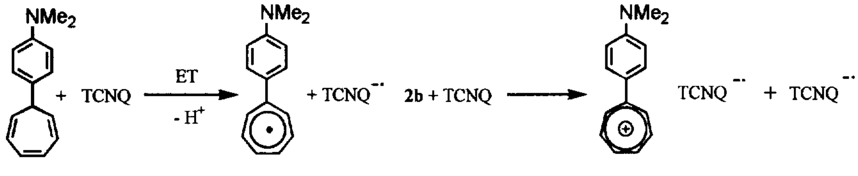
of **1a** amounts to 0.2, the chemical yield to 70 %. [11]

Quinones such as **5a** are two electron oxidants with a strongly pH dependent redox potential. In acid acetonitrile solution **1a** is oxidized by photoexcited p-benzoquinone yielding **3a** and hydroquinone at a yield of 90 % (Scheme 3). In this case, the quinone radical formed after the photoinduced electron transfer oxidizes the tropyl radical **2a** yielding hydroquinone and **3a** in acid solution.



Scheme 3 **1a** **5a** **3a**

TCNQ acts as a strong electron acceptor even in neutral solution. But, surprisingly, the formation of the tropylium ion **3b** takes place only thermally. The reaction may occur via the electron-proton-electron sequence shown in Scheme 4. According to Scheme 4 the ratio of TCNQ$^{\cdot-}$ /**3b** is 2 at the beginning and reduced later by known reactions of this radical anion (Fig. 1).[12] Immediately after mixing of **1b** and TCNQ a complex salt with the stoichiometry **1b**x2TCNQ precipitates which is slowly redissolved yielding **3b** TCNQ$^{\cdot-}$ in a 1:1 ratio.



1b **5b** **2b** **3b**

Scheme 4

In summary, this investigation clearly shows that the photooxidation of arylcycloheptatrienes both as a first step of a photoswitch and as a synthetic method can be performed. Studies with further electron acceptors and macrocycles containing cycloheptatriene components are currently in progress.

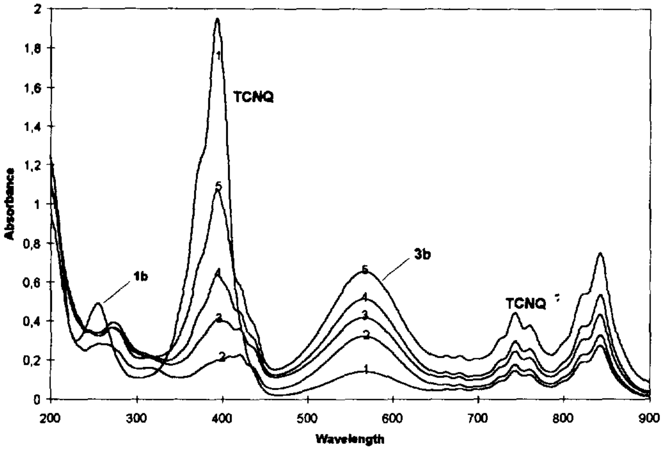


Fig. 1. UV-Vis spectrum of a deaerated solution of a 1:1 mixture of **1b** and TCNQ (0.01 M) at different time after mixing: 1 = immediately after mixing; 2 = 40 min, precipitate is formed; 3 = 60 min; 4 = 120 min; 5 = 180 min (**3b**: $\varepsilon_{565\,\mathrm{nm}}$= 35 280 $\mathrm{M^{-1}cm^{-1}}$; $\mathrm{TCNQ^{\cdot-}}$: $\varepsilon_{842\,\mathrm{nm}}$= 40 000 $\mathrm{M^{-1}cm^{-1}}$)

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