The photogeneration of aryltropylium ions: a potential photo-switch for supramolecular assemblies based on donor–acceptor interaction

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The photogeneration of aryltropylium cations with lifetimes strongly depending on the donor capacity of the aryl substituent has been achieved by photolysing the corresponding 7-methoxycycloheptatrienes 2, 3 and 4.

Switchable supramolecular assemblies such as rotaxanes[1] and catenanes[2] comprise a fascinating challenge in the field of supramolecular chemistry.[3] We are designing macrocycles[4] and rotaxanes with arylcycloheptatriene building blocks which can easily be transformed to tropylium ions by thermal hydride transfer.[5] In contrast to cycloheptatyrienes, tropylium ions are strong electron-acceptors which can be used to recognize donor partners within rotaxanes or catenanes.

Here we report on the generation of tropylium ions by photochemical heterolytic cleavage of the C–O bond in cycloheptatriene derivatives **2**, **3** and **4**. Provided the cycloheptatriene is regenerated by the fast nucleophilic attack of the methoxy ion or methanol (see Scheme 1), the acceptor can be
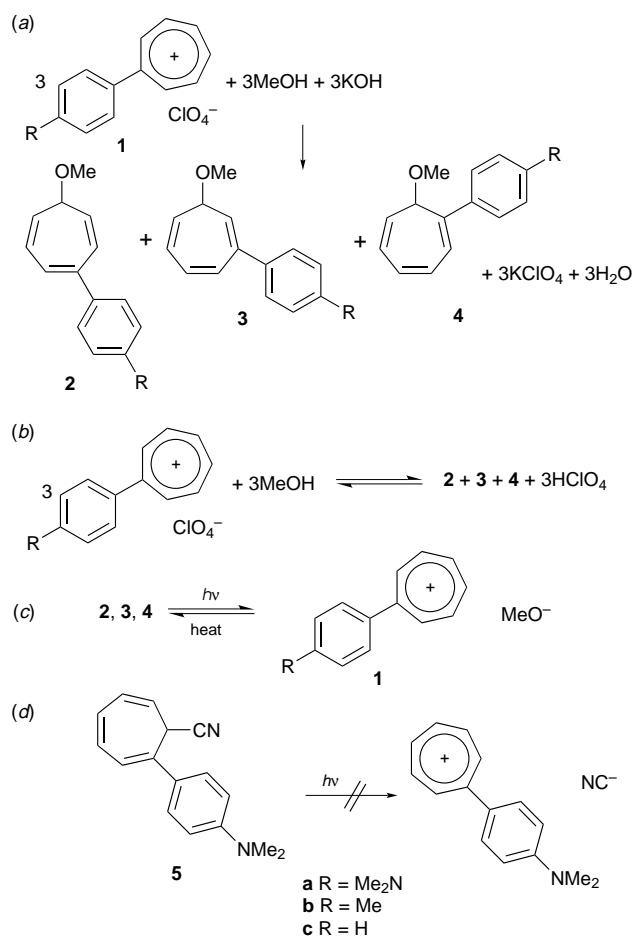

Scheme 1

switched 'on' and 'off' by a photochemical and a thermal step, respectively.

So far the only known example is the dibenzosuberenyl cation, which can be obtained by laser flash photolysis of the parent alcohol in trifluoroethanol.[6] Our design of precursors of tropylium cations is based on cycloheptatriene derivatives containing effective leaving groups and substituents capable of stabilizing tropylium ions. Halides and azide are inappropriate leaving groups because cycloheptatriene derivatives containing these groups are converted into tropylium ions upon dissolution in polar solvents.[7] In the present work CN and MeO were chosen as leaving groups and aryl groups as stabilizing substituents. 7-Methoxy-x-aryl cycloheptatrienes (x = 1, 2, 3) were prepared by the reaction of the corresponding aryl-tropylium ions with a base in methanol solution. Typically, the reaction of 4-dimethylaminophenyltropylium perchlorate **1a** with KOH results in the formation 3-(4-dimethylaminophenyl)-7-methoxycyclohepta-1,3,5-triene **2a** and the isomers **3a** and **4a** in the ratio **2a**:**3a**:**4a** = 1:1:0.7. Compound **2a** was isolated from the isomeric mixture, obtained by reaction of **1a**, by recrystallization from hexane at low temperature.

Three experiments were performed to study the photogeneration of aryltropylium ions with the aid of a ruby laser (Korad Model K1 QS2, λ = 347 nm, flash duration 20 ns) or a flashed xenon lamp (band filter 1602 and 810, Jenaer Glaswerk Schott & Gen., nominal wavelength λ_{ex} = 340–380 nm, flash duration 15 µs): (i) Compounds **2a** or **5** were irradiated in MeCN or MeOH solution. (ii) The mixture of isomers (**2**, **3** and **4**) obtained by the reaction of **1** with KOH in MeOH according to reaction (a) in Scheme 1 was irradiated *in situ*. (iii) A dilute solution of **1a** in MeOH (2×10^{-5} mol l^{-1}) was irradiated in the absence of a base. Under these conditions the equilibrium (b) in Scheme 1 is shifted almost completely to the right side, *i.e.* the solution contains the isomers **2a**, **3a** and **4a** apart from a very small amount of the tropylium ion.

Notably, apart from **5** all other cycloheptatriene derivatives yielded the tropylium ion upon UV irradiation. Obviously, CN is not as effective a leaving group as the methoxy group.

In the case of **2a** [experiment (i)] the photogeneration of **1a** according to reaction (c) in Scheme 1 was evidenced by the formation of the characteristic optical absorption of the tropylium ion (λ_{max} = 570 nm) during the flash (see Fig. 1). Simultaneously with the transient absorption a photocurrent was formed indicating the generation of ionic species (**1a** and MeO$^-$). The quantum yield Φ(ion) = 0.1 for the generation of **1a** in MeOH solution was determined† with the aid of the extinction coefficient of **1a** ε_{567} = 4.7 $\times$ 10^4 l mol^{-1} cm^{-1}. The transient absorption at $\lambda_{max} \approx$ 570 nm increased linearly with the absorbed dose per flash, indicating that the heterolytic bond cleavage in **2a** is not due to a biphotonic effect but results from a one photon excitation. Noticeably, at constant absorbed dose, the transient absorption at $\lambda_{max} \approx$ 570 nm is much weaker in MeCN than in MeOH indicating different ion yields in the two solvents. In this connection it is interesting to note that other carbenium ions were also found to be generated with higher yields in MeOH than in MeCN solution.[8]

Irradiation of the isomers **2a**, **3a** and **4a** *in situ* [experiment (ii)] also resulted in the formation of the transient absorption spectrum of **1a**.

The tropylium ion generated as described above turned out to be unusually long-lived. Compound **1a**, generated by photo-excitation of **2a** in MeOH solution [experiment (i)] disappeared according to second order kinetics: $k_2 = 2 \times 10^6$ mol^{-1} s^{-1}, corresponding to a first half-life of 0.3 s at [**1a**] $= 1.7 \times 10^{-6}$ mol l^{-1}. Obviously, the rate of decay of **1a** is determined by the neutralization reaction, **1a** + MeO$^-$ in this case. In the case of experiment (iii) the disappearance followed exactly first order kinetics with a pseudo-first order rate constant: $k_1 = 0.3$ s^{-1}. In this case the rate of disappearance is determined by the reaction of **1a** with MeOH because methoxy anions produced in the primary photolytic act are scavenged by protons [see reaction (*b*) in Scheme 1]. With aid of $k_1 = 0.3$ s^{-1}, the bimolecular rate constant $k_2 = k_1/$[MeOH] $= 1.2 \times 10^{-2}$ l mol^{-1} s^{-1} is obtained for the reaction **1a** + MeOH.

Compounds with substitutents **b** and **c** on the aryl group were examined *via* experiment (ii), *i.e.* **1b** and **1c** were converted into the corresponding isomer mixtures **2b**, **3b**, **4b** and **2c**, **3c**, **4c**,

respectively, by reaction with KOH (1 equiv.) in MeOH, and the reaction mixtures were irradiated. The transient absorption spectra recorded in these cases posses maxima at the positions expected[5] for the tropylium ions **1b** and **1c** ($\lambda = 370$ and 395 nm, respectively). The first-order lifetimes are definitely shorter than in the case of **1a**: $\tau = 270$ μs (**1b**) and 190 μs (**1c**). The large differences in the lifetimes of **1a**, **1b** and **1c** are explained in terms of an increased stability of the tropylium ion with increasing electron-donor power of the substituent at the aryl group. This assumption is substantiated by the reduction potentials measured *vs.* SCE: -0.40 (**1a**), -0.19 (**1b**) and -0.17 V (**1c**).[9]

In conclusion, the quantum yield of ion generation is large enough and the lifetime of photogenerated tropylium ions is long enough to allow intramolecular rearrangements in rotaxanes or catenanes containing arylcycloheptatriene building blocks. Concerning the applicability of such systems as photoswitches, system-optimizing appears necessary with respect to long-term performance. Regarding compound **2a**, the switch cycle can be repeated several times. However, irradiation of **2a** with 10 laser flashes (5.7×10^{-5} E l^{-1} flash^{-1}, flash duration 20 ns) reduces the intensity of the transient optical absorption due to **1a** by a factor of 2.

Footnotes

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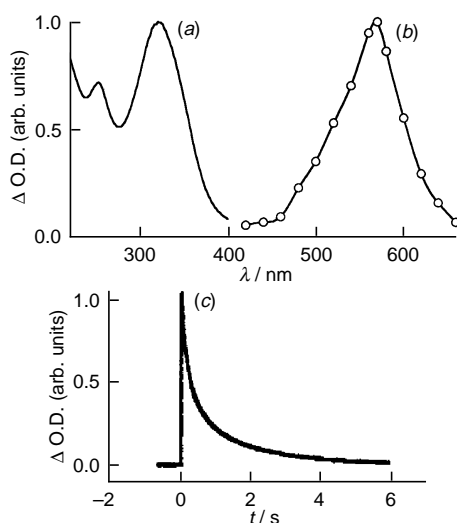9 B. Dreher, W. Abraham and F. Pragst, *J. Prakt, Chem.,* 1983, **325**, 104.

Fig. 1 (*a*) Optical absorption spectrum of **2a** in MeOH; (*b*) transient absorption spectrum recorded 250 ms after irradiation of **2a** in MeOH with a 15 μs flash ($\lambda_{ex} = 340$–380 nm); (*c*) decay of the transient absorption at 570 nm