ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 128 (1999) 75–83

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Reduction of aryl tropylium ions by thermal hydride transfer or by photochemical reactions

Dirk Jacobi [a], Werner Abraham [a,*], Uwe Pischel [a], Reinhard Stößer [a], Wolfram Schnabel [b]

[a] *Humboldt-Universität zu Berlin, Institut für Chemie, Hessische Str. 1-2, D-10115 Berlin, Germany*

[b] *Hahn-Meitner-Institut Berlin GmbH, Bereich Physikalische Chemie, Glienicker Str. 100, D-14109 Berlin, Germany*

Received 13 April 1999; accepted 7 July 1999

Abstract

The reduction of aryl-substituted tropylium cations in deaerated acetonitrile solution at room temperature can be achieved by two methods: (a) thermal hydride transfer from the heterocyclic compounds 9,10-dihydro-10-methylacridine, $AcrH_2$, and 2,4,6-triphenyl-4H-pyran, TPPH, to *p*-methoxyphenyl tropylium perchlorate, **1**, and *p*-dimethylaminophenyl tropylium perchlorate, **2**, that affords regioselectively aryl-substituted cycloheptatrienes and (b) photoinduced electron transfer from $AcrH_2$, TPPH, 10,10′-dimethyl-9,9′-bisacridane, $(AcrH)_2$, or 2,2′,4,4′,6,6′-hexamethyl-4,4′-bi-(4H-pyran), $(TMP)_2$, to **1** and **2**.

The light-induced reduction was studied with the aid of steady state photolysis and laser flash spectroscopy. A mechanism involving the photoionization of $(AcrH)_2$ is proposed. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Tropylium salts; Bitropyls; Photochemistry; Electron transfer; Hydride transfer

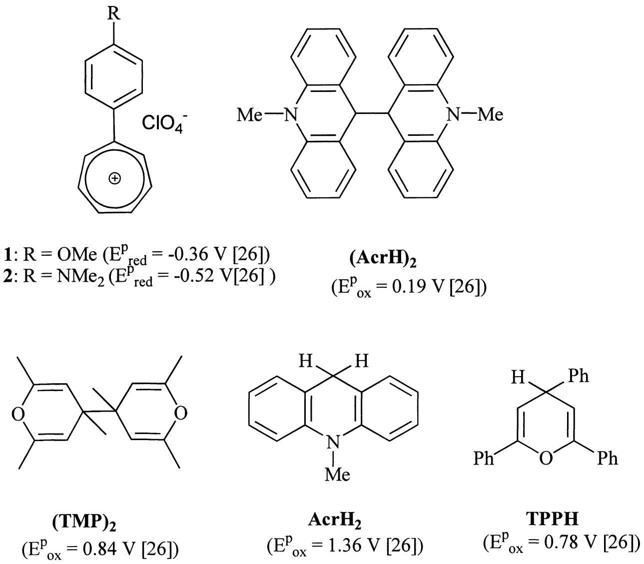
---

1. Introduction

The thermal reduction of tropylium ions resulting in the formation of bitropyls has been well known for a long time [1]. However, so far, the photochemical reduction has not yet been investigated. The photochemical transformation of tropylium cations into cycloheptatrienes is of special interest since the two compounds vary significantly in several properties such as shape, acceptor strength and color which may be useful in order to change the properties of molecules such as calixarenes [2] containing the tropylium subunit in response to light.

The compounds studied in this work are presented in Chart 1. The potentials (SCE) given in brackets are peak potentials. [26]

The salts *p*-methoxyphenyl tropylium perchlorate, **1**, and *p*-dimethylaminophenyl tropylium perchlorate, **2**, that possess different reduction peak potentials [3] served as model compounds for aryl-substituted tropylium salts and the compounds 9,10-dihydro-10-methylacridine, $AcrH_2$, 2,4,6-triphenyl-4H-pyran, TPPH, 10,10′-dimethyl-9,9′-bisacridane, $(AcrH)_2$, and 2,2′,4,4′,6,6′-hexamethyl-4,4′-bi-(4H-pyran) $(TMP)_2$ served as electron donors. Acetonitrile solutions of the reactants were irradiated continuously for the sake of product analysis; moreover, they were subjected to flash photolysis to detect intermediates. The detection of paramagnetic species by ESR spectroscopy was attempted.



1: R = OMe (E^p_{red} = -0.36 V [26])
2: R = NMe_2 (E^p_{red} = -0.52 V[26])

$(AcrH)_2$
(E^p_{ox} = 0.19 V [26])

$(TMP)_2$
(E^p_{ox} = 0.84 V [26])

$AcrH_2$
(E^p_{ox} = 1.36 V [26])

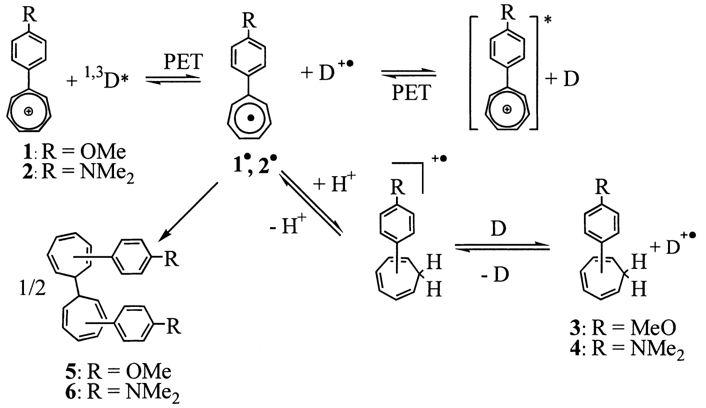
TPPH
(E^p_{ox} = 0.78 V [26])

Chart 1. Compounds used in Photoreduction studies.

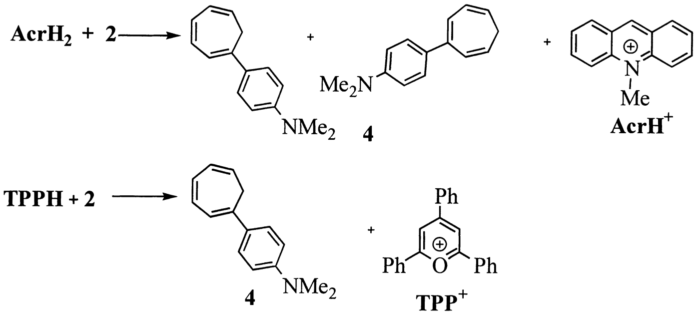
---

* Corresponding author.
E-mail address: abraham@chemie.hu-berlin.de (W. Abraham)

PII: S1010-6030(99)00154-9



Scheme 1.



Scheme 2.

Regarding the photoreduction of a substituted tropylium ion via electron transfer from a donor, two pathways are feasible depending on whether the tropylium ion or the donor is photoexcited. As is illustrated in Scheme 1, both pathways result in the formation of the cycloheptatrienyl type radical, **1**$^\bullet$, **2**$^\bullet$.These radicals, principally, can undergo the following reactions: (i) protonation of the radicals **1**$^\bullet$ and **2**$^\bullet$, respectively, gives the corresponding radical cations. Subsequent transfer of an electron from the donor molecule D, being in the ground state, results in the formation of the stable cycloheptatrienes **3** and **4**; (ii) two radicals of type **1**$^\bullet$ and **2**$^\bullet$ combine yielding bitropyl, **5** or **6**, the dimers of **3** and **4**, respectively.

Experiments were carried out to study both the thermal and the photochemical reduction of aryl-substituted tropylium ions and the results are reported below.

2. Results and discussion

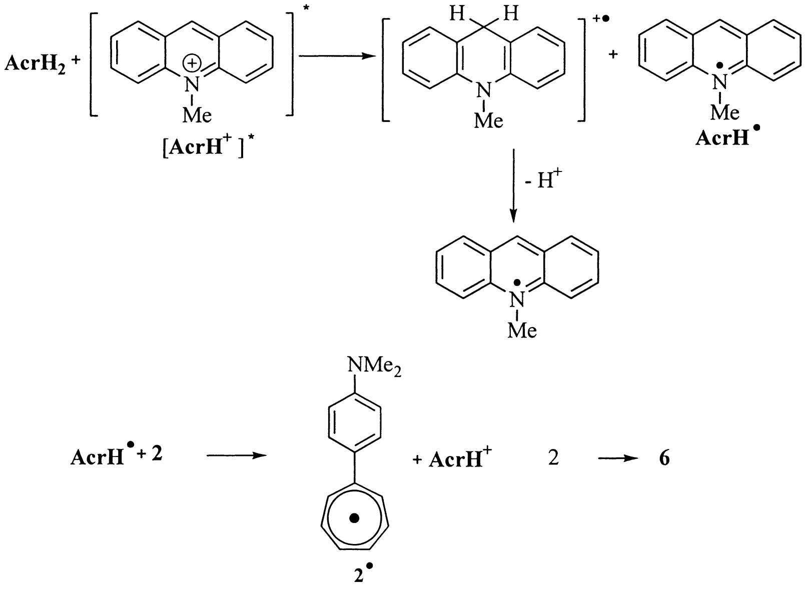
2.1. Thermal reaction

Both $AcrH_2$, and TPPH are capable of reducing **1** and **2**, respectively, at room temperature but only at a slow rate. This was evidenced by product analysis with the aid of high pressure liquid chromatography (HPLC) using authentic samples for calibration. The reaction products expected according to Scheme 2, i.e. the aryl-substituted cycloheptatrienes and the *N*-methylacridinium ion, $AcrH^+$, and the triphenyl pyrylium ion, TPP^+, respectively, were identified. The bimolecular rate constant of the reaction of $AcrH_2$ with **2** was determined to be $2.7 \times 10^{-2}\,M^{-1}\,s^{-1}$ by following the decay of **2** by means of UV–VIS spectroscopy.

The reduction of the tropylium ions is assumed to involve hydride transfer because intermediate products indicative of electron transfer were not detected. Such intermediate products would be *N*-methylacridinyl radicals, in the case of $AcrH_2$, or triphenyl pyranyl radicals, in the case of TPPH. The former radicals are expected to couple readily, and thus, form the dimer $(AcrH)_2$, while the latter radicals are rather stable [4], and therefore, should be detectable by ESR. However, neither $(AcrH)_2$ could be observed nor was it possible to detect the triphenyl pyranyl radicals by ESR measurements. Actually, the occurrence of thermal electron transfer is unlikely because it is highly endergonic as estimated on the basis of the reduction peak potentials of the donor and acceptor compounds listed in Chart 1.

A statistical attack of hydride ion on the substituted tropylium ion would lead to an isomer mixture of 14.3% of the 7- and 28.6% of each of the 1-, 2- and 3-isomers. But only the 1- and 3-isomers were found. Obviously, the thermodynamically more stable isomers are formed exclusively. Notably, there are significant differences between TPPH and $AcrH_2$. When TPPH reacts with **1** or **2**, only the corresponding 1-isomer is formed. In contrast, when $AcrH_2$ reacts with **1** or **2**, the 1- and 3-isomers of **3** and **4** are formed in a 1 : 1 ratio.

The reduction of **1** by TPPH has been carried out on a preparative scale (see Section 3) to obtain the



Scheme 3.

1-(4-methoxyphenyl)cycloheptatriene which is difficult to be synthesized via photochemical or thermal hydrogen shift of the corresponding 7-substituted derivative [5].

Concluding this paragraph, it should be pointed out that, to the authors' best knowledge, the present work provides evidence for the first time for the formation of 1- or 3-aryl-substituted cycloheptatriene by hydride transfer.

2.2. Photochemical reactions

2.2.1. Photochemical reactions involving monomeric electron donors

2.2.1.1. System AcrH$_2$/2. The *N*-methylacridinyl radical is capable of reducing the tropylium cation **2** [6]. Therefore, for the photoreduction of **2**, the generation of *N*-methylacridinyl radicals via photoinduced electron transfer is desirable. In this connection, the work of Fukuzumi et al. [7] is noteworthy. These authors have shown that optically excited electron acceptors such as $[Ru(bpy)_3]^{2+}$ sensitize the formation of *N*-methylacridinyl radicals from AcrH$_2$.

Therefore, we studied the analogous electron transfer reaction from AcrH$_2$ to optically excited **2** and observed that, upon excitation of the tropylium salt **2** ($\lambda_{exc} = 578$ nm) in the presence of AcrH$_2$, only a very slow reaction proceeded. This can be explained by the very short lifetime of the excited tropylium ions [8]. At the applied AcrH$_2$ concentrations ranging from 5×10^{-4} to 5×10^{-5} M, only a very low amount of the excited state of **2** is quenched by AcrH$_2$. On account of the thermal reduction described above, it is, therefore, senseless to initiate an electron transfer via the excited state of the tropylium cation even by using higher quencher concentrations.

Optically excited AcrH$^+$ can also serve as an electron acceptor to generate *N*-methylacridinyl radicals from AcrH$_2$. Due to the thermal reaction between **2** and AcrH$_2$ (see Scheme 2), always, a small concentration of AcrH$^+$ is present in a solution containing **2** and AcrH$_2$ indicated by the low optical density at 360 nm ($OD_{360\,nm} < 0.05$). Upon excitation of a solution containing 5×10^{-3} M AcrH$_2$ and 1×10^{-3} M **2** at 436 nm, the decomposition of **2** and the formation of AcrH$^+$ occur as was evidenced with the help of HPLC. It turned out that AcrH$^+$ was formed to the same extent as **2** was consumed. Simultaneously, the formation of the bitropyl **6** was proven. Under this condition, the photoreaction is about one order of magnitude faster than the thermal reaction. Accordingly, the product of the hydride transfer (**4**) was not found.

A feasible reaction mechanism is shown in Scheme 3. According to the oxidation potential of the *N*-methylacridinyl radical (−0.46 V [9]) and the reduction potential of **2** (−0.53 V [6]), the reaction of *N*-methylacridinyl radical +**2** is weakly endergonic. Since the magnitude of the oxidation potentials of the acridinyl radical and of the radical **2**$^\bullet$ are almost equal, AcrH$^+$ ions are likely to react with **2**$^\bullet$ also. However, this reaction, apparently, is unimportant because **2**$^\bullet$ radicals readily combine and form **6**.

2.2.1.2. Systems TPPH/1 and TPPH/2. The system TPPH/1 was irradiated at $\lambda_{exc} = 405$ nm where mainly TPP$^+$ absorbs. TPP$^+$ was not added purposely, but it was formed to a very small extent by thermal hydride transfer during the preparation of the solution. The irradiation resulted in the consumption of **1** and the simultaneous formation of TPP$^+$ and a mixture of regio-isomers of **5**. The products were identified by HPLC. The rate of the consumption of **1** was, under the chosen conditions, about 10 times faster than that of the dark reaction. Apparently, a mechanism similar to that proposed for the system AcrH$_2$/2 applies to

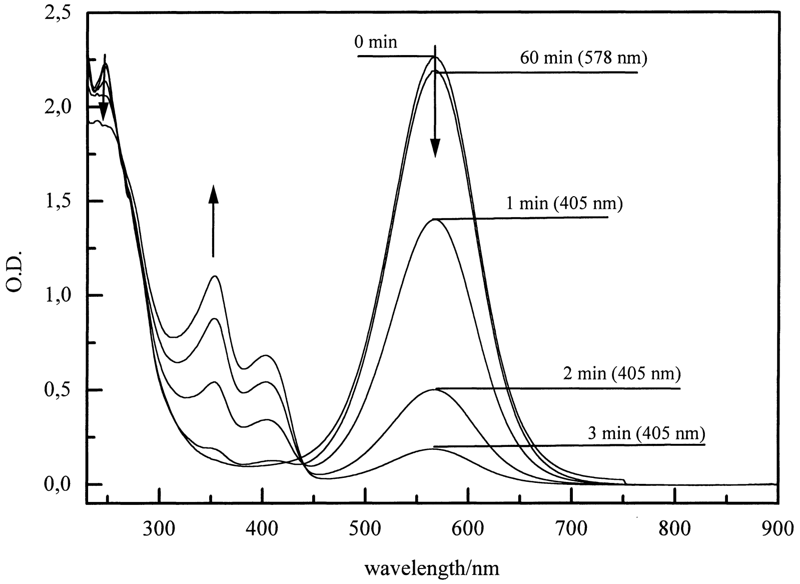


Fig. 1. Photolysis of the system TPPH/2 in deaerated acetonitrile solution at $\lambda_{inc} = 578$ and 405 nm. [TPPH] = [**2**] = 7×10^{-5} M. Optical absorption spectra recorded after various irradiation times as indicated in the graph.

the system TPPH/1. In other words, $(TPP^+)^*$ reacts with TPPH. The resulting radical cation deprotonates forming the triphenyl pyranyl radical ($E_{ox} = -0.51$ V [6]). The latter reduces **1** ($E^{p}_{red} = -0.36$ V) in an exergonic reaction. Radicals $\mathbf{1}^{\bullet}$ generated in this way combine and form **5**.

Upon irradiation of the system TPPH/2 at $\lambda_{exc} = 578$ nm, where **2** absorbs the light, the latter was decomposed, and simultaneously, the TPP^+ ion was formed, as was inferred from the build-up of an absorption band at 405 nm. However, as is illustrated in Fig. 1 also, in this case, the photoreaction initiated by the excitation of **2** is too slow to compete significantly with the thermal reduction. To achieve a substantial reduction of **2**, the system TPPH/2 was initially irradiated at $\lambda_{exc} = 578$ nm and subsequently at $\lambda_{exc} = 405$ nm. In this way, the TPP^+ ions generated in the first stage and excited in the second stage oxidized TPPH, and $TPPH^{+\bullet}$ was formed, apart from $TPP^{\bullet}$. Actually, a mechanism analogous to that proposed for the system TPPH/1 becomes operative here.

The photoreaction accomplished in this way is much faster than the thermal hydride transfer. Accordingly, **4** is not formed in this case.

2.2.2. Photochemical reactions involving dimeric electron donors

2.2.2.1. System $(AcrH)_2$/2

2.2.2.1.1. Laser flash experiments in the absence of **2**. In order to estimate the role of $(AcrH)_2$ in the photoreduction of **2**, the behavior of excited $(AcrH)_2$ has to be studied.

Upon direct excitation of $(AcrH)_2$ with 347 nm laser flashes, *N*-methylacridinyl radicals are formed. This is concluded from the transient absorption spectrum shown in Fig. 2a recorded at the end of the 20 ns flash. It exhibits an absorption band at 510 nm which is attributed to the *N*-methylacridinyl radical [10]. The assignment of the radical is also supported by the finding that the ratio of the absorption at 360 nm ($AcrH^+$, see below) and 510 nm (acridinyl radical) is drastically increased in the presence of oxygen due to the reaction of the radical with oxygen. Notably, after the irradiation in an oxygen saturated solution, a permanent absorption change at 400 nm was detected indicating the formation of *N*-methylacridone via the reaction of the *N*-methylacridinyl radical with oxygen [11].

As mentioned above, the spectrum in Fig. 2a possesses an absorption band at 360 nm which is assigned to the $AcrH^+$ ion. Both the absorption band at 360 nm and that at 510 nm increased almost linearly with the absorbed dose per flash, i.e. $\Delta OD \propto D_{abs}{}^{1.1}$, indicating that the photoionization results from monophotonic excitation. $AcrH^+$ is very likely to be formed upon the decomposition of the radical cation $(AcrH)_2{}^{+\bullet}$ generated by the photoionization of $(AcrH)_2$. Reportedly, $(AcrH)_2{}^{+\bullet}$ decomposes rapidly [12]. Notably, the formation of charged species during the flash was confirmed by photoconductivity measurements. $AcrH^+$ ions decay in a second-order reaction (see inset of Fig. 2a) with a bimolecular rate constant $k_2 = 1.3 \times 10^9\ M^{-1}\,s^{-1}$. Since solvated electrons formed in acetonitrile solution are very short-lived, it seems that the bimolecular decay of $AcrH^+$ involves a reaction with another anionic species, i.e. with monomeric and/or dimeric radical anions of acetonitrile. But these species absorb light in the wavelength range between 500 and 1500 nm only weakly [13] and were, therefore, not detectable in this work.

When the experiments were performed in methanol solution, the transient absorption of the solvated electron around 630 nm [14] (see Fig. 3) was observed apart from the absorption of the radical and the cation.

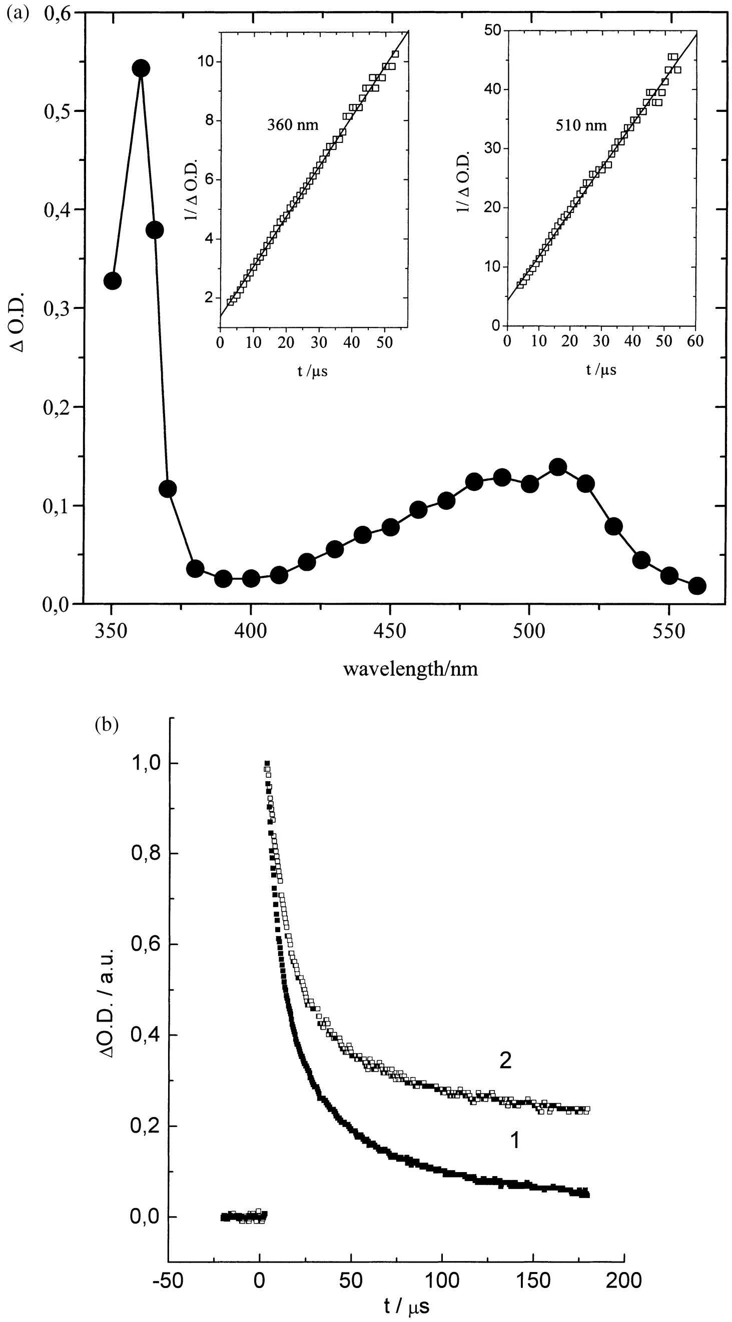


Fig. 2. (a) Transient absorption spectrum observed upon laser-flash photolysis of $(AcrH)_2$ (1.4×10^{-4} M) in deaerated acetonitrile solution at $\lambda_{inc} = 347$ nm. Insets: second-order plots of the decay at 360 and 510 nm. (b) Kinetic traces at 360 nm observed after the flash photolysis ($\lambda_{inc} = 347$ nm) of $(AcrH)_2$ (1.4×10^{-4} M) in deaerated acetonitrile solution: 1, without **2**; 2, in the presence of **2** (10^{-5} M).

According to the kinetic scheme represented by Eqs. (1)–(3), the decay of the acridinyl radicals by the dimerization reaction (2) is superimposed by the formation of the *N*-methyl acridinyl radical by the reaction of $AcrH^+$ with the equivalent of an electron (Eq. (3)).

$$(AcrH)_2^{+\bullet} \rightarrow AcrH^+ + AcrH \qquad (1)$$

$$2AcrH^\bullet \xrightarrow{k_1} (AcrH)_2 \qquad (2)$$

$$AcrH^+ + e \xrightarrow{k_2} AcrH^\bullet \qquad (3)$$

Immediately after the flash, three species are formed, the concentrations of which are equal: $[AcrH^+] = [AcrH^\bullet] =$ [electron equivalent]. Accordingly, the decay of $AcrH^\bullet$ follows Eq. (4):

$$\frac{-d[AcrH^\bullet]}{dt} = 2k_1[AcrH^\bullet]^2 - k_2[AcrH^+]^2 \qquad (4)$$

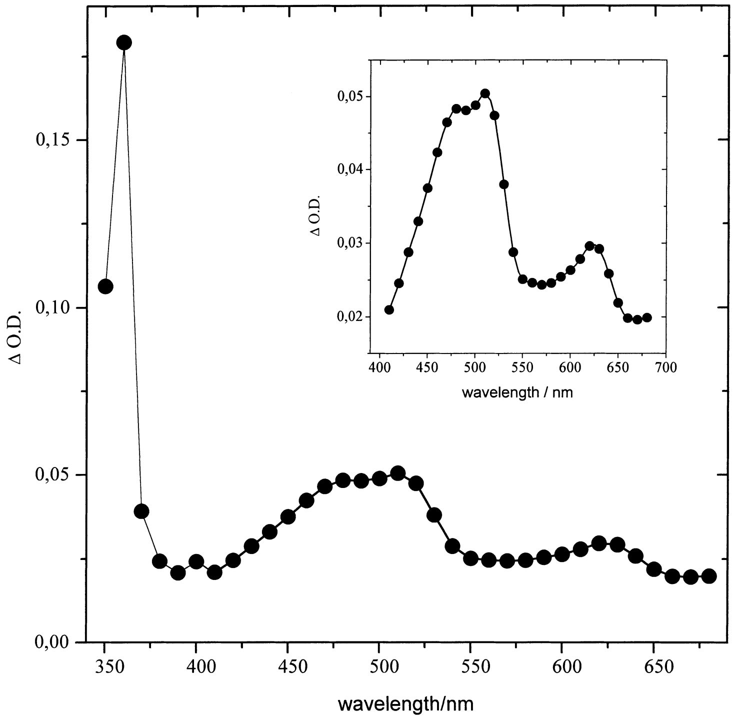


Fig. 3. Laser-flash photolysis of $(AcrH)_2$ in deaerated methanol solution at $\lambda_{inc} = 347$ nm. Transient absorption spectrum recorded at the end of the 20 ns flash.

Eqs. (3) and (4) were fitted [15] to the second-order decay of the kinetic trace measured at 510 nm (see inset in Fig. 2a). Using a molar extinction coefficient $\varepsilon = 44\,000\ M^{-1}\ dm^{-1}$ of the unsubstituted acridinyl radical [16] and the separately measured rate constant of the decay of $AcrH^+$ (see above), a bimolecular rate constant of the radical dimerization reaction $2k_1 = 2.7 \times 10^9\ M^{-1}\ s^{-1}$ was obtained. This value is in an excellent agreement with that one reported by Hammond et al. [10].

In order to find out whether excited singlet or triplet states are involved in the photoionization of $(AcrH)_2$, it was checked whether the transient absorption spectrum undergoes changes when 1,3-cyclohexadiene (10^{-1} M) is present in the solution. Actually, the triplet energy of $(AcrH)_2$ is not known, but it should be close to that of $AcrH_2$ (E_T ca. 286 kJ mol^{-1} [17]). Therefore, 1,3-cyclohexadiene should be a suitable triplet quencher in this case, since its E_T is equal to 222 kJ mol^{-1} [18]. However, quenching was not observed, and therefore, it is concluded that the photoionization occurs from the excited singlet state.

The quantum yields of ion formation are $\Phi(\text{ion}) = 0.25$ and $\Phi(\text{ion}) = 0.30$ in acetonitrile and methanol solution, respectively.

2.2.2.1.2. Laser flash experiments in the presence of 2. Upon irradiation of an acetonitrile solution containing both $(AcrH)_2$ and **2** with 347 nm laser flashes, the light was mainly absorbed by $(AcrH)_2$. The transient absorption spectrum formed during the flash is very similar to that observed in the absence of **2**, i.e. it exhibits the bands of the $AcrH^+$ ion and of the *N*-methylacridinyl radical at 360 and 510 nm, respectively. Kinetic traces recorded at 360 nm are shown in Fig. 2b. It is seen that, in the presence of **2**, the decay rate is slower than in its absence. As **2** and $AcrH^+$ compete for the reaction with solvated electrons, the decay rate of $AcrH^+$ is reduced. On the other hand, the absorption of **2** at 560 nm is bleached and the bleaching is faster than the decay of $AcrH^+$. Consequently, it is assumed that **2** is reduced by reaction with both solvated electrons and/or radical anions of solvent molecules and acridinyl radicals. Due to the strong bleaching in the wavelength range from 500 to 600 nm, the decay of the acridinyl radicals in the presence of **2** cannot be analyzed.

2.2.2.1.3. Steady state photolysis

2.2.2.1.3.1. Excitation at 280 nm. The irradiation of $(AcrH)_2$ in the presence of **2** generated $AcrH^+$ ions and dimers **6**, both being formed at equal yields. These findings are in accordance with the results obtained by the flash photolysis experiments (see Section 2.2.2.1.2), which revealed the formation of the $AcrH^+$ ion and the *N*-methylacridinyl radical. **6** is thought to be the product of the combination of two $\mathbf{2}^\bullet$ radicals. The latter are formed by reaction of **2** ions with *N*-methylacridinyl radicals or anionic species, i.e. solvated electrons and/or radical anions of the solvent.

2.2.2.1.3.2. Excitation at 280 and 405 nm. In this case, an acetonitrile solution containing $(AcrH)_2$ and **2** was briefly irradiated at 280 nm to generate a small amount of $AcrH^+$.

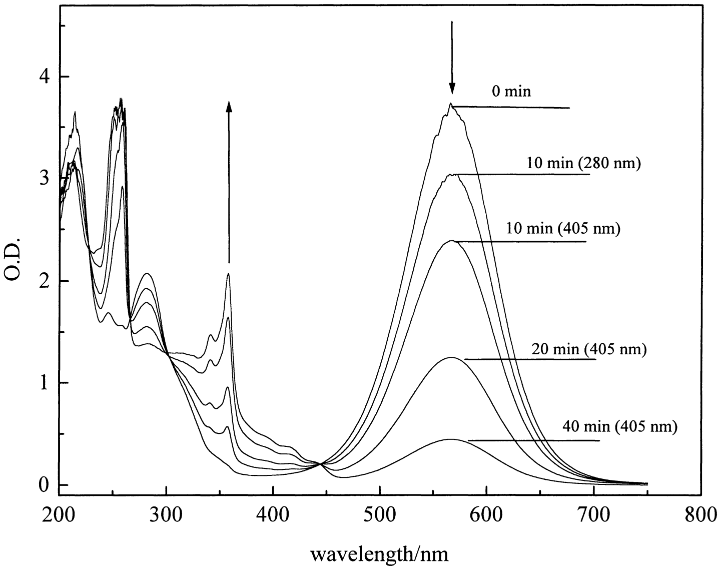


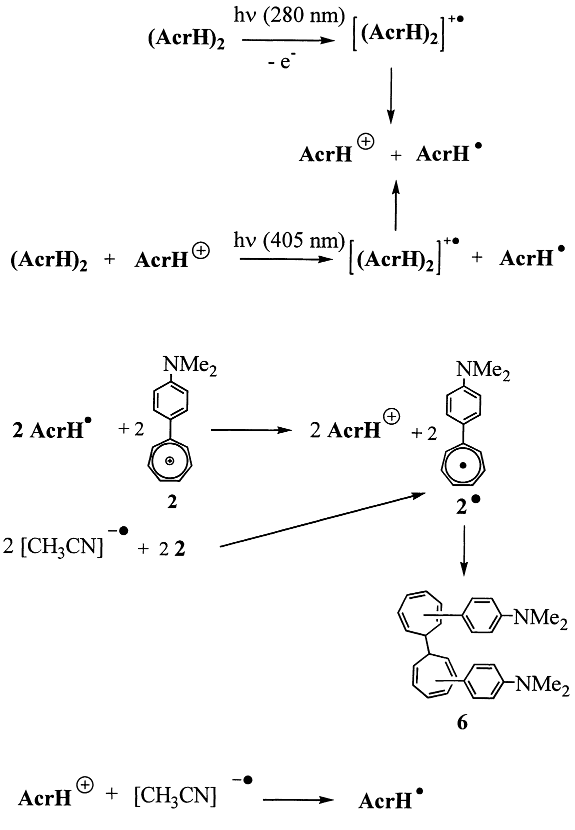
Fig. 4. Photolysis of the system $(AcrH)_2$/2 in deaerated acetonitrile solution ($[(AcrH)_2] = 5 \times 10^{-5}$ M); $[\mathbf{2}] = 10^{-4}$ M) at $\lambda_{inc} = 280$ nm and $\lambda_{inc} = 405$ nm, respectively. Optical absorption spectra recorded after various irradiation times as indicated in the graph.

Subsequently, the irradiation was continued at 405 nm. As can be seen from Fig. 4, the optical absorption bands of compound **2** that peaked at 275 and 560 nm decreased with increasing irradiation time, and simultaneously, the absorption bands of $AcrH^+$ that peaked at 260 and 360 nm were formed.

A reaction mechanism explaining why the consumption of **2** is correlated to the formation of $AcrH^+$ is proposed in Scheme 4.

The important process in this mechanism is the reaction of the electronically excited ion $(AcrH^+)^*$ with $(AcrH)_2$ that produces the radical cation $[(AcrH)_2]^{+\bullet}$. The spontaneous decomposition of the latter results in the formation of the *N*-methylacridinyl radical and the $AcrH^+$ ion. The acridinyl radical reacts with **2** and the coupling of radicals $\mathbf{2}^\bullet$ generated in this way leads to the formation of **6**. Another minor reaction route ending up in the formation of **6** consists of the reaction of anionic species such as $[CH_3CN]^{-\bullet}$, formed by photoionization, with **2**.

It is interesting to note that the irradiation of an acetonitrile solution containing $AcrH^+$ (5.5×10^{-5} M) and $(AcrH)_2$ (1.0×10^{-4} M) at 405 nm in the absence of an oxidant such as **2** did not cause the decomposition of the reactants. This indicates that *N*-methylacridinyl radicals generated by the decomposition of $[(AcrH)_2]^{+\bullet}$ combine thus regenerating $(AcrH)_2$.



Scheme 4.

2.2.2.1.4. ESR spectroscopic evidence for radical **2**. The ESR spectrum shown in Fig. 5 was recorded upon the irradiation of a solution containing **2** and *tert*-butylbenzene in 1,1,1,3,3,3-hexafluoropropane-2-ol HFIP (80/20 = v/v) in the cavity of the ESR spectrometer with white light emitted by a high pressure mercury–xenon lamp.

The same spectrum was also obtained by photo-induced electron transfer from $(AcrH)_2$ to **2** in dioxane/HFIP (80/20 = v/v). The recorded spectrum is identical to the spectrum of radical $\mathbf{2}^\bullet$ simulated on the basis of the hyperfine coupling constants given in the caption of Fig. 5.

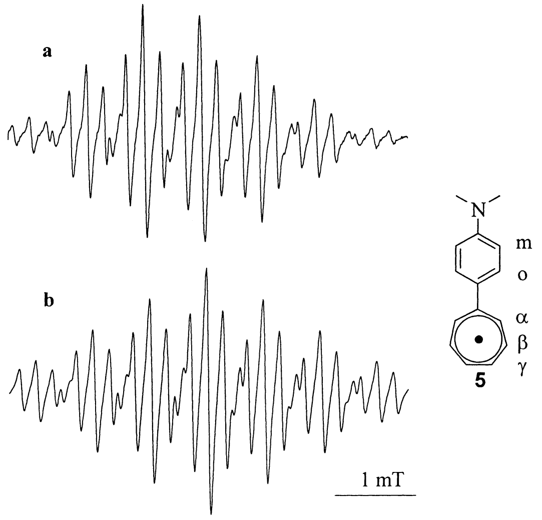


Fig. 5. (a) ESR-spectrum of the radical $2^\bullet$ ($g = 2.0039$) generated by the photolysis of **2** in the presence of *t*-butylbenzene. (b) Simulated ESR-spectrum of $2^\bullet$ using the hfs-parameters: $a_\alpha = 1.43$ mT; $a_o = 0.718$ mT; $a_\beta = 0.223$ mT; $a_m = 0.201$ mT (no significant coupling with N is assumed).

2.2.2.1.5. System $(TMP)_2/2$ This system exhibits a behavior quite similar to that of the system $(AcrH)_2/2$, i.e. continuous irradiation of an acetonitrile solution containing $(TMP)_2$ and **2** at $\lambda_{exc} = 280$ nm results in the formation of **6** and the 2,4,6-trimethyl pyrylium ion. A feasible reaction mechanism is presented in Scheme 5.

2.3. Conclusions

1. Aryl tropylium cations are transformed into 1-aryl-1,3,5-cycloheptatrienes by thermal hydride transfer using 10-methyl-9,9-dihydroacridine or 2,4,6-triphenyl-4H-pyran as hydride donors.
2. Aryl tropylium ions, being in an electronically excited state, are reduced by electron transfer from dihydroacridine or 4-H-pyran compounds. The reduction results in the formation of aryl-substituted bitropyls.
3. Aryl tropylium ions, being in the ground state, are reduced by suitable radicals such as the 10-methylacridinyl radical or the triphenyl pyranyl radical which are generated by direct photolysis of 10,10′-dimethyl-9,9′-biacridine or 2,2′,4,4′,6,6′-hexamethyl-bi-(4H-pyran) or by the reaction of these compounds with electronically excited *N*-methyl acridinium or triphenyl pyrylium ions.

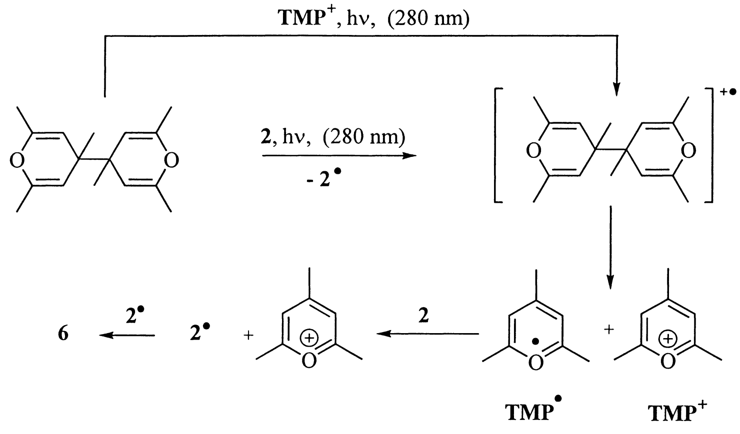
3. Experimental section

General: UV–VIS: Shimadzu UV-2101 PC spectrophotometer. –NMR: Bruker DPX 300 (300 MHz).

Steady state photolysis experiments were carried out in acetonitrile solution deaerated by argon bubbling at a substrate concentration ranging from 5×10^{-4} to 10^{-3} M (**1** or **2**) and hydride donor concentrations ranging from 5×10^{-4} to 5×10^{-3} M of $AcrH_2$ or TPPH, respectively. The two electron donors were applied in concentrations of $[(AcrH)_2] = 1.5 \times 10^{-4}$ M and $[(TMP)_2] = 5 \times 10^{-4}$ M in the photoreduction of **2** (1×10^{-4} M). The solutions were irradiated in 1 cm quartz cuvettes using a 500 W high pressure mercury lamp, operated in conjunction with a metal interference filter (Carl Zeiss Jena) or an Oriel monochromator (model 77200), or in quartz tubes using a Rayonet photoreactor. Laser flash photolysis was realized with the aid of a ruby laser (Korad Model K1 QS2, $\lambda = 347$ nm, flash duration 20 ns).

Photoionization experiments: deaerated acetonitrile solutions of $(AcrH)_2$ (2.2×10^{-4} M) were excited with the aid of the ruby laser.

ESR experiments: the generation of radicals was carried out by irradiation of the deaerated solutions placed in a quartz tube within the cavity of the ESR-spectrometer (ERS-300, ZWG) with the unfiltered light of a 800 W



Scheme 5.

mercury–xenon lamp. Simulation of the spectrum was done with the aid of the program Compar 2.

3.1. Quantum yields

The rate constant of tropylium ion decay was calculated by the tangent method from plots of conversion versus the time of irradiation. The concentration of tropylium ions was obtained by measuring the optical absorption of **1** at 435 nm ($\varepsilon = 22\,500\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$) and that of **4** at 567 nm ($\varepsilon = 46\,840\,\mathrm{dm^3\,mol^{-1}\,cm^{-1}}$). The absorbed irradiation dose was determined with the aid of the ferric oxalate actinometer. The quantum yield of ion formation in laser flash experiments was determined with the aid of the benzophenone/naphthalene-actinometer [19].

HPLC analysis was performed using RP 18 phases, $MeCN/H_2O$ 80 : 20, buffer triethylamine/H_3PO_4 (pH = 2.7) as mobile phase and a diode array detector (Shimadzu SPD-M10A).

3.2. Chemicals

Acetonitrile (HPLC grade) was obtained from Riedel de Haen. 2,4,6-triphenyl pyrylium tetrafluoroborate was received from Merck and recrystallized from ethanol. The acceptors **1**, **2** [20] and *N*-methylacridinium perchlorate [21], and the donors 2,4,6-triphenyl-4H-pyran [22], 9,10-dihydro-10-methylacridine [23], 10,10′-dimethyl-9,9′-bisacridane [24] and 2,2′,4,4′,6,6′-hexamethyl-4,4′-bi-(4H-pyran) [25] were synthesized according to prescriptions reported in the literature.

x,*x*′-disubstituted bitropyls **4** used as calibration standard were available from earlier studies [6].

1-(4-Methoxyphenyl)cycloheptatriene (**3**): 230 mg (7.2×10^{-4} mol) 2,4,6-triphenyl-4H-pyran and 330 mg (1.11×10^{-3} mol) 4-methoxyphenyl tropylium perchlorate were dissolved in 100 ml deaerated acetonitrile. After stirring for 48 h in the dark under argon at room temperature, the solvent was removed under reduced pressure. The oily residue was treated with 100 ml of *t*-butyl-methylether. The precipitate consisting of 2,4,6-triphenyl pyrylium perchlorate and the remaining tropylium salt was filtered off. Evaporation of the *t*-butyl-methylether solution yielded 140 mg of the oily raw product (98% based on 4H-pyran).

Freezing of a methanol solution gives 110 mg (77%) of the crystalline 1-(4-methoxyphenyl)cycloheptatriene m.p. = 42°C; literature 34°C [5].

Acknowledgements

Financial support was given by the Fonds der Chemischen Industrie.

References

[1] W.T. Browie, M. Feldman, J. Chem. Phys. 71 (1967) 3696.
[2] V. Wendel, W. Abraham, Tetrahedron Lett. 38 (1997) 1177.
[3] B. Dreher, W. Abraham, F. Pragst, J. Prakt. Chem. 325 (1983) 104.
[4] S. Niizuma, N. Sato, H. Kawata, Y. Suzuki, T. Toda, H. Kokubun, Bull. Chem. Soc. Jpn. 58 (1985) 2600.
[5] W. Abraham, C. Csongár, E. Henke, D. Kreysig, J. Prakt. Chem. 321 (1979) 117.
[6] D. Jacobi, W. Abraham, U. Pischel, L. Grubert, W. Schnabel, J. Chem. Soc., Perkin Trans. 2 (1999) 1241.
[7] S. Fukuzumi, S. Mochizuki, T. Tanaka, J. Phys. Chem. 94 (1990) 722.
[8] W. Abraham, B. Dreher, K. Buck, D. Kreysig, J. Prakt. Chem. 324 (1982) 925.
[9] P. Hapiot, J. Moiroux, J.-M. Savéant, J. Am. Chem. Soc. 112 (1990) 1337.
[10] A.T. Poulus, G.S. Hammond, M.E. Burton, Photochem. Photobiol. 34 (1981) 169.
[11] S. Fukuzumi, M. Ishikawa, T. Tanaka, J. Chem. Soc., Perkin Trans. 2 (1989) 1037.
[12] S. Fukuzumi, T. Kitano, M.J. Ishikawa, J. Am. Chem. Soc. 112 (1990) 5631.
[13] I.P. Bell, M.A.J. Rodgers, J. Chem. Soc., Faraday Trans. 73 (1977) 315.
[14] L.M. Dorfman, in: J. Hart (Ed.), Adv. Chem. Ser., vol. 50, 1965, p. 36, ACS, Washington DC.
[15] Program pro Fit 5.1.2 ppc, Quantum Soft, Zurich.
[16] P. Neta, J. Phys. Chem. 83 (1979) 3096.
[17] K. Kano, B. Zhou, S. Hashimoto, Bull. Chem. Soc. Jpn. 60 (1987) 1041.
[18] C.G. Hatchard, C.A. Parker, Proc. R. Soc. London, Ser. A 235 (1956) 518.
[19] A. Eckardt, S. Nespurek, W. Schnabel, Ber. Bunsenges. Phys. Chem. 98 (1994) 1325.
[20] C. Jutz, F. Voithenleitner, Chem. Ber. 97 (1964) 29.
[21] S. Fukuzumi, S. Koumitsu, K. Hironaka, T. Tanaka, J. Am. Chem. Soc. 109 (1987) 305.
[22] A.F. Blinokhatov, O.V. Markovtseva, M.N. Nikolaeva, Chem. Heterocycl. Compd. 28 (1992) 266.
[23] A.K. Colter, G. Saito, F.J. Sharom, Can. J. Chem. 55 (1977) 2741.
[24] A.M. Grigorovski, A.A. Simeonov, I.K. Feldman, Zh. Obshch. Khim. 21 (1951) 589.
[25] A.T. Balaban, C. Bratu, C.N. Rentea, Tetrahedron 20 (1964) 265.
[26] D. Jacobi, Ph.D. Thesis, Humboldt-University, Berlin, 1998.