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1,4-Photoaddition of Maleic Anhydride to Chrysene

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The photo *Diels-Alder* reaction of maleic anhydride with chrysene yields chryseno[4,5-efg]isobenzofuran-4,6-dion (VI). Heavy atom experiments using xenon as an external perturber show that the reaction occurs via the lowest singlet excited state of chrysene. Hydrogen is abstracted from the primary *Diels-Alder* adduct IV by the solvent CH_2Cl_2 possibly in a two-step mechanism. The reaction presents a new type of photoreaction, its mechanism possibly follows a scheme not considered so far in photochemistry.

(Keywords: Chrysene; Maleic anhydride; Mechanism of photoaddition; 1,4-Photoaddition)

1,4-Photoaddition von Maleinsäureanhydrid an Chrysen

Die Photo-*Diels-Alder*-Reaktion von Maleinsäureanhydrid mit Chrysen ergibt Chryseno[4,5-efg]-isobenzofuran-4,6-dion (VI). Schweratomexperimente mit Xenon als äußerer Störer zeigen, daß die Reaktion vom niedrigst angeregten Singulettzustand des Chrysens ausgeht. Die Abstraktion von Wasserstoffatomen aus dem primären *Diels-Alder*-Addukt IV durch das Lösungsmittel CH_2Cl_2 folgt möglicherweise einem Zweistufenmechanismus. Die Reaktion stellt einen neuen Typ von Photoreaktion dar; möglicherweise folgt sie einem Mechanismus, der in der Photochemie neuartig ist.

Introduction

Two types of *thermal* 1,4-cycloaddition reactions of maleic anhydride with polycyclic aromatic hydrocarbons (*PAH*) are known:

i) addition to *PAH*s of the acene series yielding adducts of type I[1].

ii) addition to *PAH*s containing a peripherical *cisoid* C_4-unit yielding adducts of type II[2]. Since adducts II are readily dehydrogenated to aromatic systems, the reaction is useful for the synthesis of *PAH*s. The thermal 4 + 2 addition of maleic anhydride to *PAH*s in the

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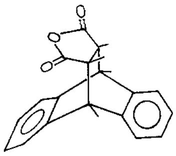
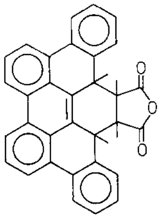
presence of dehydrogenating agents yielding aromatic dicarboxylic acid anhydrides is well known as "benzogenic *Diels-Alder* reaction"[3].



I



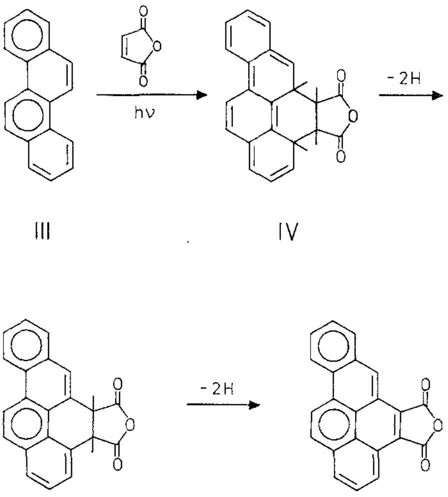
II

Up to now, only the first of these two reaction modes is known to occur also *photochemically*[4].

Both types of the thermal 1,4-cycloaddition correlate very well with the butadienoid character orders[5] of the reactive zone as shown in ref.[6] for mode (i) and in refs.[5,7] for mode (ii). Various *PAH*s which do not undergo the thermal addition of maleic anhydride exhibit a much higher butadienoid character order in their first electronically excited state than in their ground state[8]. Hence, it can be assumed that the addition of maleic anhydride to the electronically excited states of these *PAH*s could follow the same reaction pathway as the thermal benzogenic *Diels-Alder* reaction[2]. The photochemical experiments described below were therefore carried out in order to test this reasoning and, possibly, to extend the scope of this reaction principle. In fact, we have recently found that the benzogenic *Diels-Alder* reaction can also take place photochemically[9,10]; this is a novel type of photoreaction of maleic anhydride with *PAH*s. However it can not be cogently decided whether the photochemical reaction mechanism is identical to or different from that of the thermal reaction, since the first intermediate could neither be isolated nor characterized.

Results

In order to clarify some details of the complex mechanistic questions that arise from this new type of photoaddition, chrysene (III), which does not undergo a thermal benzogenic *Diels-Alder* reaction, was taken as the model *PAH*. In the photoreaction a dicarboxylic acid anhydride was expected to be formed as a final product which could then be readily decarboxylated to the well characterized benzo[a]pyrene.



III IV

V VI

The experimental conditions were optimised in the course of these experiments (see experimental part). Experiments carried out in the presence of air gave a maximum yield of 18% of VI after an irradiation time of 2.5 hours. The overall yield decreased to 2% after 20 hours[10] (Fig. 1). However, the overall yield increased to 27% after 20 hours if the experiment was carried out in an Argon atmosphere.

A Solidex glass filter (Duran 50) was used to cut off the radiation of the mercury lamp at wavelenghts $< 270\,\mathrm{nm}$; no charge-transfer complex between chrysene and maleic anhydride could be detected by careful UV absorption studies under the conditions used for the photochemical experiments; therefore it is assumed that only the *PAH* was excited.

Although the fluorescence spectrum of chrysene remains unchanged in the presence of maleic anhydride, the latter acts as a fluorescence quencher. The intensity and lifetime of fluorescence decrease linearly with increasing quencher concentration according to a hyperbolic *Stern-Volmer* law as required by a dynamic quenching mechanism. The bimolecular rate constant of fluorescence quenching was found to be $k_q = 9.9\ 10^9\,\mathrm{l\,mol^{-1}s^{-1}}$. So far it could not be decided whether the observed fluorescence quenching is due to electron transfer or to the formation of the primary product of the photoreaction.

The quantum yield for the overall reaction III → VI was found to be $4.4\ 10^{-3}$.

According to *Kasha*'s rule, the reaction can occur via the S_1 or T_1 excited state of chrysene. In order to decide which of these states is involved, the reaction was carried out in the presence of an external heavy atom perturber which increases the rate of intersystem crossing ($S_1 \rightarrow T_1$). The dependence of the overall yield of the photochemical reaction on the presence of the external perturber can be used as a probe to find out which excited state is the reactive one. Several common external heavy atom quenchers like alkyl halides or sodium iodide gave no clear results since complications arose from the photolysis of these compounds. Therefore, xenon was used as an external

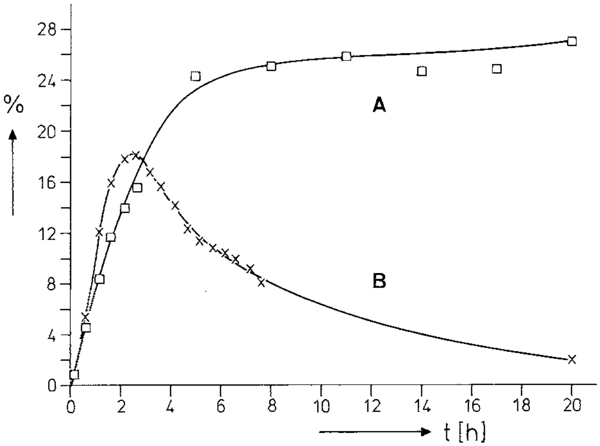


Fig. 1. Time dependence of the overall yield of VI in the presence of Ar (*A*) and air (*B*)

heavy atom perturber. This is a further example[14] of the application of xenon as a perturber in a photochemical mechanistic study in condensed phase. Xenon is an ideal heavy atom quencher since it shows no chemical reactivity and absorbs at very short wavelengths; additionally it is also easy to handle and gives a strong heavy atom effect. Experiments carried out in the presence of Xe (1 atm) gave a decrease of 40% in the overall yield of the photochemical reaction. Thus it must be concluded that S_1 is the reactive state.

In the reaction scheme a primary intermediate IV is formulated. This is the actual *Diels-Alder* adduct, which is thought to be in equilibrium with the starting materials. This intermediate, however, could not be isolated from the reaction mixture using TLC and HPLC. The longest absorption wavelength of the chromophoric system of IV was calculated by the *PPP*-CI method to lie at 609 nm[11]. No significant absorption at this wavelength could be detected in the crude reaction product. In an attempt to isolate an intermediate of type IV the following olefinic compounds were used as dienophiles:

3,4-dichloro-2,5-furandione
1*H*-pyrrole-2,5-dione
2-butenedioic acid dimethyl ester (*Z*)
2-butenedioic acid dimethyl ester (*E*)
2-butenedioyl dichloride (*E*)
2-chloro-2-butenedioyl dichloride (*E*)
2,3-dicyano-2-butenedioic acid dimethyl ester (*E*)

However, photoaddition to chrysene was only observed with the cyclic dienophiles whereas openchain olefines proved unreactive. Furthermore, the primary adduct could not be isolated from any of the systems studied.

A further intermediate V, arising from IV by the abstraction of two hydrogen atoms, is assumed in the reaction scheme given above. This compound was detected in the mass spectrum of the crude reaction product when 3,4-dichloro-2,5-furandione was used as the dienophile: the dominating peak in the mass spectrum (*m*/e 358) corresponds to the analogous monochloro adduct ($C_{22}H_{11}ClO_3$).

Further abstraction of two hydrogen atoms from V gives compound VI which was isolated in pure form. The yield of VI proved to be independent in the temperature range from —80 °C to +40 °C. Up to now VI has not been described in the literature; moreover, the photochemical synthesis of VI should be superior to standard procedures[3].

The four hydrogen atoms are abstracted probably in two steps by the solvent CH_2Cl_2; this was concluded from the formation of HCl, CH_3Cl, and CH_4.

Discussion

As pointed out in the introduction there are sound reasons to assume that the photochemical mechanism for the reaction described above does not differ from that of the thermal benzogenic *Diels-Alder* reaction. It is then to be expected that the reaction follows an electrocyclic pathway corresponding to a 4 + 2 cycloaddition starting from the first excited singlet state of the *PAH*. Although it is confirmed that the photoreaction does start from the first excited singlet state of chrysene, no further evidence for the proposed reaction pathway could be obtained. In particular our attempts to evaluate the stereochemistry of the primary intermediate IV using dienophiles of the general structure $XYC{=}CXY$ were completely abortive due to the unreactivity of these olefines with chrysene. On the other hand, however, there is no experimental fact contradicting an electrocyclic 4 + 2 cycloaddition. Since usually the initial steps in photoreactions differ significantly from those of thermal reactions so, to our knowledge, the reaction reported above would be the first exception to this rule.

There is not enough data available concerning the role of butadienoid character orders in the chemistry of excited *PAH*s in order to discuss the reaction in these terms. Therefore we prefer the use of *Fukui*'s frontier orbital concept[13] to show that the most simple and straightforward way to form the photoproducts corresponds to an electrocyclic addition[12].

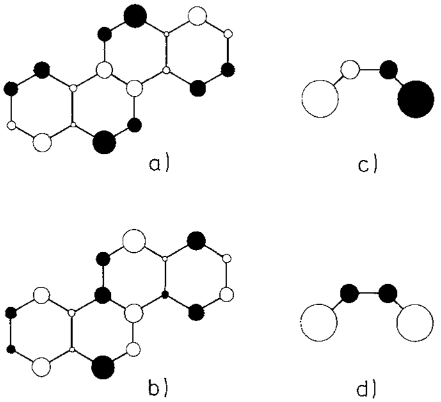


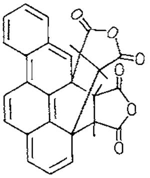
Fig. 2. LCAO pattern of the highest occupied orbital of chrysene in its ground state (*a*) and in its S_1-α state (*b*); HOMO (*c*) and LUMO (*d*) of ground state butadiene

Fig. 2 shows the LCAO-pattern[11,12] of the highest occupied orbital of chrysene in its ground state (a), the main CI-contribution to the highest occupied orbital of chrysene in its S_1-α state (b), and for comparison, the HOMO (c) and LUMO (d) of ground state butadiene. All the drawings are based on *PPP*-CI-calculations. According to the frontier orbital interpretation[13] the peripherical *cisoid* C_4-units of chrysene are not expected to undergo a *Diels-Alder* reaction in the ground state but in the S_1-α state. In line with this expectation the excited chrysene undergoes the *Diels-Alder* reaction.

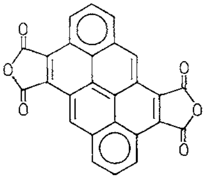
The excitation of chrysene to its S_1-α state transforms the LCAO pattern in the peripherical *cisoid* C_4-units so that it resembles the HOMO of butadiene in its ground state, for which thermal *Diels-Alder* reactions are well understood[13]. To our knowledge the possibility of generating ground state properties in subunits of molecules by the absorption of light has not been considered so far.

Probably, the lack of resonance stabilisation makes the first adduct IV elusive. Consequently it undergoes either a *retro Diels-Alder* reaction yielding the starting materials or hydrogen abstraction to give the identified aromatizised products V and VI. We further postulate that the hydrogen abstraction occurs in two steps via the intermediate V. This is supported by the experiments with 3,4-dichloro-2,5-furandione where the monochloro analogue of V is, according to the mass spectrum, probably the main reaction product. A more detailed evaluation of the mechanism (stereochemistry and formation of IV by one or two steps, orbital symmetry rules) would require the isolation and subsequent investigation of IV.

No products of double addition of maleic anhydride to chrysene (VII or VIII), either formed in a manner similar to the reported thermal reaction of dibenzo[b,n]perylene with maleic anhydride[2], or in a double addition to two different regions of chrysene yielding the anthanthrene derivative have been found.



VII



VIII

We have already reported similar reactions using picene as *PAH*[9]. We assume that in this case the same reaction mechanism as outlined above is valid since chrysene and picene have the same topology.

Acknowledgement

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Experimental

Equimolar amounts of chrysene and fresh sublimed maleic anhydride (5-7 mmol each) are dissolved in 600 ml CH_2Cl_2. Argon is bubbled through the solution which is irradiated with a Philips HPK 125 W/L lamp (Duran 50 filter) for 20 hours. According to the UV spectrum the crude reaction product contains 27% of VI (under Argon; in the presence of air we find a maximum yield of 18% after 2.5 hours, after 20 hours the overall yield decreases to 2%).

The overall quantum yield was found to be $4.4 \cdot 10^{-3}$. The sample is concentrated to dryness (10^{-2} Torr) and the residue washed with water until the washings are neutral. After drying, the residue is chromatographed (Kieselgel 60, solvent: CH_2Cl_2). A red fraction is eluted which, after concentrating to dryness and sublimation in vacuo at 300 °C/10^{-2} Torr yields chryseno[4,5-efg]isobenzofuran-4,6-dione (VI) (16%), red needles, m.p.: 333 °C (uncorr.).

$C_{22}H_{10}O_3$. Calc. C 81.98, H 3.13, O 14.89.
Found C 81.73, H 3.59, O 14.48.

Mass spectrum (70 eV; *m*/e): 322 (97%), 250 (100%).

IR (KBr; cm^{-1}): 1860, 1780 (anhydride).

UV[benzene; λ_{max}^{nm} ($\lg \varepsilon$)]: 469 (3.86), 424 (3.77), 401 (3.53), 380 (3.16), 334 (4.32), 323 (4.32), 277 (4.57).

Further proofs of the structure of VI are:

a) the UV spectrum in 2% KOH is a slightly shifted spectrum of benzo[a]pyrene;

b) the fragmentation pattern in the mass spectrum is characteristic of an anhydride;

c) decarboxylation of VI yields benzo[a]pyrene. [Under the conditions used (sodalime, 350 °C) no change of the molecular skeleton has been described in similar cases.]

The fluorescence spectra for the *Stern-Volmer* plot were measured with a Spex Fluorolog 1902. The samples were freed from oxygen by repeatedly freezing and pumping ($\lambda_{exc.} = 320$ nm).

Nanosecond time resolved fluorescence decays were measured with a single-photon counting instrument, equipped with Ortec electronics and an Ortec multichannel analyser and an Applied Photophysics optical unit with a gated air-filled lamp ($\lambda_{exc.} = 322$ nm).

2 mol HCl per mol reaction product were detected by titration with 0.1 *N* NaOH. CH_4 and CH_3Cl were observed in the gas chromatogram of the irradiated solutions.

For the heavy atom experiments the solutions after degassing, were equilibrated with an atmosphere of argon and xenon respectively and irradiated with light from a glass filtered mercury lamp (HPK 125) using 1 cm Beckman type cuvettes with attached Westef Stopcocks.

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