

## Short Communication

## Micelle-directed regioselective photodimerization of 9-hydroxymethyl-anthracene

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(Received January 15, 1981; in revised form March 6, 1981)

## 1. Introduction

The photodimerization (Fig. 1) of anthracene and its 9-substituted derivatives (1) as well as the photochemical and thermal back reactions of the dimers (2), (3) have been the subjects of numerous preparative, mechanistic and theoretical studies during the last years [1 - 18]. On irradiation, 9-substituted anthracenes (1) usually form only the so-called head-to-tail (h-t) photodimers (2). A few cases of head-to-head (h-h) photodimerizations have been reported in very recent publications [17, 18]. From earlier investigations only intramolecular h-h photodimerizations of 9-9'-linked dianthracenes [14, 15] and some cases of mixed h-h photodimerizations of anthracenes bearing substituents of differing donor and acceptor properties in the 9-position [8] are known. However, photodimers of anthracenes are also susceptible to photochemical and thermal splitting into monomers. The thermal cleavage of h-h photodimers is known to be much faster than that of h-t dimers [8]. The isolation of h-h photodimers is therefore difficult, even if h-h photodimerization takes place efficiently.

In some cases of photoaddition reactions, enhancements of regioselectivities by solubilizing the reagents in micelles have recently been observed [19 - 21]. In the present study therefore, both the photodimeriza-

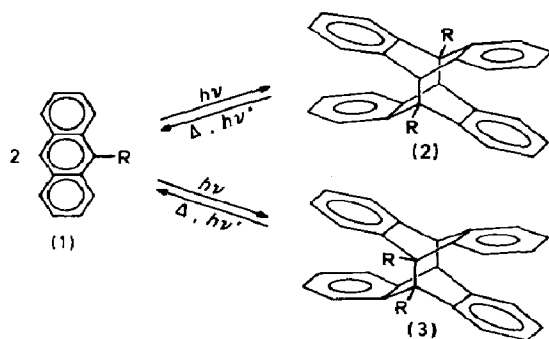


Fig. 1. The photodimerization of anthracene and its 9-substituted derivatives.

tion of 9-hydroxymethylanthracene (1) ( $R \equiv \text{CH}_2\text{OH}$ ) and the thermal back reaction were investigated in diethyl ether and in aqueous solutions of sodium dodecylsulphate micelles. Micellar-solubilized 9-hydroxymethylanthracene molecules are expected to be arranged in such a way that the polar OH groups are directed to the polar regions of the micellar "surfaces" while the aromatic parts of the molecules trend towards the hydrocarbon-like interior of the micelles. Under conditions where the micelles are occupied by more than one molecule, the formation of h-h photodimers is expected to be favoured by this preorientation.

## 2. Experimental procedure

### 2.1. Substances

9-Hydroxymethylanthracene (Ega) was recrystallized three times from a 1:4 mixture of chloroform:petroleum ether (boiling point, 35 - 38 °C). Diethyl ether (Merck, Uvasol) and sodium dodecylsulphate (Merck, p.a.) were used without further purification. Surfactant solutions were prepared using demineralized water.

### 2.2. Irradiation in homogeneous solution

0.5 g (0.0024 mol) 9-hydroxymethylanthracene dissolved in 300 ml diethyl ether was irradiated in a nitrogen atmosphere for 3 h at 297 K with Solidex-filtered light from a high pressure mercury lamp in an apparatus described elsewhere [22]. The progress of the reaction was followed with UV spectroscopy until the peaks of the educt at  $\lambda > 300$  nm had disappeared. A white precipitate was formed which was filtered and recrystallized from ethanol.

### 2.3. Irradiation in micellar solution

300 ml of a solution of sodium dodecylsulphate ( $5 \times 10^{-2}$  M) were saturated with 9-hydroxymethylanthracene (about  $2 \times 10^{-3}$  M) and irradiated for 3 h as described in Section 2.2. Calcium chloride was added until the calcium salt of the amphiphile precipitated together with the photoproduct. The precipitate was filtered and washed five times with 100 ml diethyl ether at about 5 °C. The ether phase was dried with magnesium sulphate and the solvent was evaporated at 5 - 10 °C.

### 2.4. Measurements

UV spectra were recorded on a Beckman Acta M VII spectrophotometer. Nuclear magnetic resonance (NMR) spectra were measured on a Bruker Spectrospin WP 80 NMR spectrometer in deuteriochloroform against tetramethylsilane.

## 3. Results

After irradiation of solutions of 9-hydroxymethylanthracene in diethyl ether under nitrogen and work-up of the precipitated photoproducts by recrystallization, photodimers in high yields (80% - 90%) were obtained,

which were identified by NMR and UV spectroscopy. Compared with the NMR spectrum of the educt the spectrum of the product showed the following differences. The aromatic protons of the educt appeared as three groups of multiplet signals between 7.5 and 8.5 ppm whereas the product spectrum showed only two groups of multiplets between 6.8 and 7.2 ppm. A doublet signal of the  $\text{CH}_2$  group protons appeared at 5.7 ppm for the educt and at 4.9 ppm for the product. An additional singlet signal appeared at 4.5 ppm in the spectrum of the product. Chemical shifts in this ppm region have been reported [8] for the bridgehead protons of 9-substituted anthracene photodimers. In the UV spectrum of the product the "anthracene" peaks of the educt at  $\lambda > 300$  nm had disappeared. This spectroscopic evidence is in agreement with an assignment of the isolated product to the structure of the h-t photodimer (2) ( $\text{R} \equiv \text{CH}_2\text{OH}$ ).

After storage of the irradiated solution overnight at room temperature the UV peaks of the educt at  $\lambda > 300$  nm reappeared at 8% of their intensity before irradiation, indicating the presence of an unstable photoproduct that is capable of a thermal back reaction. This experiment was repeated at different temperatures and the kinetics of the back reaction were followed with UV spectrophotometry. An activation energy of  $110 \text{ kJ mol}^{-1}$  was determined (Fig. 2) for this back reaction. The unstable photoproduct did not appear in the NMR spectrum when the recrystallization procedure described earlier was applied. However, after work-up at somewhat lower temperatures (about  $10^\circ\text{C}$ ) without recrystallization, a new small singlet NMR signal appeared at 5.1 ppm with less than 10% of the intensity at 4.5 ppm. Since no coupling constant is expected for equivalent protons, these results are taken as evidence in the identification of the unstable photoproduct as the h-h photodimer (3) ( $\text{R} \equiv \text{CH}_2\text{OH}$ ) (compare with ref. 18). This assignment is supported by the value for the activation energy determined for the back reaction, which is significantly lower than values published for analogous reactions of several h-t photodimers [23].

On irradiation of 9-hydroxymethylanthracene in micellar solutions (0.05 M sodium dodecylsulphate), much higher yields of the h-h photodimers (30% - 60%) were obtained as indicated by the ratio of the integrals of the

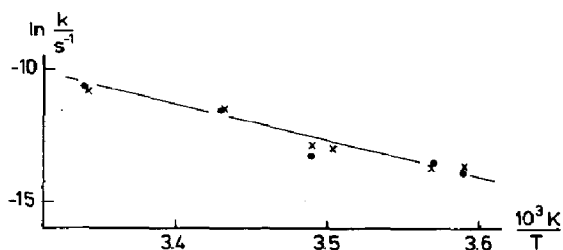


Fig. 2. An Arrhenius diagram for the thermal back reaction of h-h photodimers of 9-anthrylmethanol formed in diethyl ether (x) and in 0.05 M sodium dodecylsulphate (●). The kinetics were measured in diethyl ether.

NMR signals at 5.1 and 4.5 ppm and by the amount of the thermally labile part of the photoproduct determined by measuring the intensity of the reappearing UV peaks of the educt. Also, the decay kinetics of the thermally labile part of the photoproduct coincided with that of the h-h photodimers obtained from irradiation in homogeneous solution when the product was transferred from the micellar solvent to diethyl ether (Fig. 2).

#### 4. Conclusion

A dramatic increase in the ratio of h-h to h-t photodimers of 9-hydroxymethylanthracene is observed on substituting a homogeneous solvent (diethyl ether) with a micellar solution (0.05 M sodium dodecylsulphate). This demonstrates the feasibility of exploiting preorientational effects of the micellar structure for selective syntheses.

#### Acknowledgments

The author is grateful to Professor G. von Büнау for helpful discussions and critical reading of the manuscript. I thank Mr. R. Waffenschmidt for technical assistance and Mr. R. Boy for measuring the NMR spectra.

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