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Water-in-oil microemulsions as microreactors to control the regioselectivity in the photocycloaddition of 9-substituted anthracenes

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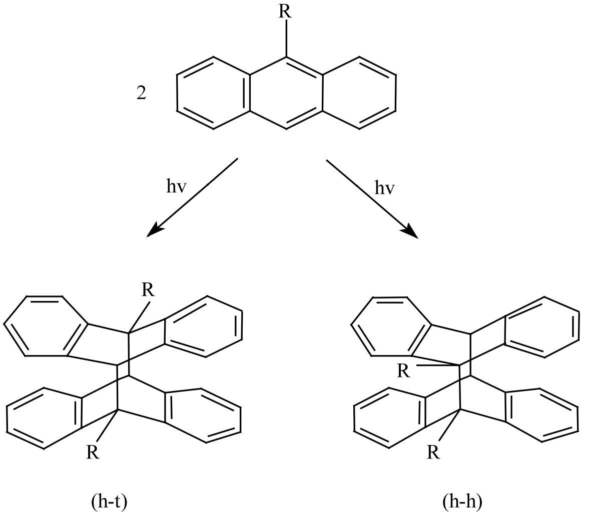
Abstract—The photocycloaddition of five 9-substituted anthracenes [$AnCH_2N^+(CH_3)_3Br^-$ (**1**), $AnCH_2COONa$ (**2**), $AnCH_2OH$ (**3**), $AnCOCH_3$ (**4**), $AnCH_3$ (**5**), An = 9-anthryl] incorporated in water-in-oil microemulsions prepared from sodium bis(2-ethylhexyl) sulfosuccinate (AOT), methylene chloride and water has been investigated. While irradiation of the above substrates in methylene chloride, and **5** in the microemulsions also, mainly gave rise to their head-to-tail (h-t) photocyclomers, photoirradiation of the samples of **1**–**4** incorporated in the microemulsions almost exclusively yielded the head-to-head (h-h) photocyclomers. These observations were interpreted in terms of the preorientation of the substrate molecules at the interface of the water pool in the microemulsions. © 2002 Elsevier Science Ltd. All rights reserved.

Selectivity in organic phototransformations continues to be one of the main topics of current interest. Of the various approaches, the use of organized and constrained media as microreactors to control reaction pathways has shown considerable promise.[1,2] Water-in-oil (W/O) microemulsions are heterogeneous, thermodynamically stable systems of nanosized domains of water dispersed within an immiscible organic (oil) phase and stabilized by a surfactant shell.[3,4] The water microdroplets, often called the 'water pool', provide a hydrophilic nanospace, while the organic component forms a hydrophobic continuous phase. These microemulsion systems have the ability to solubilize normally slightly water-soluble substrates. The hydrophilic substrates are solubilized primarily in the water pool, whereas hydrophobic molecules exist in the organic phase or at the interface of the water pool. Thus, W/O microemulsions have been used as 'microreactors' for many specific reactions.[5,6] However, the use of microemulsions to direct the regioselectivity of a photochemical reaction has rarely been reported. In previous work,[7] we were able to control successfully the regioselectivity in photocycloaddition of anthracene derivatives by incorporation in water-swollen Nafion membranes. Since the microreactors provided by W/O microemulsions are analogous to those of Nafion membranes, in the present work we extend our study on the photochemical reaction of anthracenes to microemulsions.



Scheme 1. Photocycloaddition of 9-substituted anthracene.

Irradiation of 9-substituted anthracenes in organic solution typically results in cycloaddition of the aromatic rings at the 9,10-positions to yield head-to-tail (h-t) cyclomers (Scheme 1), although evidence for the concomitant formation of head-to-head (h-h) cyclomers has been obtained in some instances.[7,8] This regioselec-

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Table 1. Chemical shifts (ppm $CDCl_3$) of the bridgehead protons and h-t/h-h ratios of the photocyclomers of **1**–**5**

Chemical shifts of bridged protons			Ratios of h-t to h-h	
Compound	$\delta_{\text{h-t}}$	$\delta_{\text{h-h}}$	CH_2Cl_2	Microemulsion
1	4.38	4.52	65/35	0/100
2	4.80	5.13	83/17[a]	8/92
3	4.52	4.84	68/32	10/90
4	5.77	5.63	74/26	38/62
5	4.00	4.56	58/42	57/43

[a] The h-t/h-h ratio in ethyl ether solution.

tivity was rationalized in terms of the electrostatic and steric effects of the substituents. When anthracene bearing an ionic or a polar substituent is incorporated within W/O microemulsions, one might expect that the substrate would be concentrated at the interface of the water pool and the molecules would be arranged in such a way that the anthracene moiety is located in the hydrophobic organic phase with the polar substituent towards the water pool. This preorientation would favor the formation of h-h photocyclomers and the enhancement of the local concentration would increase the quantum yield of the photocycloaddition. We found that photoirradiation of 1–3 incorporated in microemulsions indeed almost exclusively leads to the h-h photocyclomers in high quantum yields.

We irradiated **1**–**5** in homogeneous solutions or in W/O microemulsions in a Pyrex reactor. Prior to irradiation, the samples were degassed with nitrogen for 15 min. A 500 W high-pressure mercury lamp was used as the light source. The photocycloaddition process was monitored by UV absorption spectroscopy. The h-h and h-t cyclomers were separated by using a Perkin–Elmer HPLC with a SUPELCOSIL™ LC-18 column, and methanol/water was used as the eluting solvent. Of particular interest was the ratio of h-t to h-h cyclomers, which was determined both by HPLC measurement and the ^{1}H NMR spectroscopy of the product mixture. The ratios obtained by these two methods were consistent with each other. Irradiation of the 2.4×10^{-3} M degassed solutions of **1**–**5** in methylene chloride led to the formation of the h-t and h-h cyclomers with the former as the main products. Table 1 gives the ratios of the h-t to h-h cyclomers for **1** and **3**–**5**. Since the solubility of **2** in methylene chloride is very limited, the photocycloaddition of this compound was carried out in ethyl ether, and the ratio of the h-t to h-h cyclomers is also given in Table 1. For all the substrates, the yields of the photocyclomers are close to 100% on the basis of the consumption of the starting materials. The structure proposed for the products as the [4π+4π] cyclomers rests mainly on their ^{1}H NMR spectra, which are in close agreement with those reported in the literature.[7–9] The assignment of the h-t and the h-h photocyclomers relies on the chemical shifts of the bridgehead protons in their ^{1}H NMR spectra. It has been established[7–9] that the chemical shifts of the bridgehead protons for the h-h cyclomers appear at lower regions compared with those for the corresponding h-t cyclomers. However, it was found that the bridgehead methine protons of the h-h cyclomer of **4** resonate at higher field than that of the h-t cyclomer, because the bridgehead proton of the h-t cyclomer is deshielded by the adjacent carbonyl group. The chemical shifts of the bridgehead protons in the h-t and h-h cyclomers of **1**–**5** are summarized in Table 1.

The situation for the photocycloaddition of **1**–**4** in microemulsions is completely different. The microemulsions used in the present study were simply prepared by sonicating the three-component mixture of water, methylene chloride and the surfactant sodium bis(2-ethylhexyl)sulfosuccinate (AOT) at 30°C for 20 min. The overall concentration of AOT in the three-component mixture was 5×10^{-2} M, and the molar ratio of water to AOT was 15. **1**–**5** could be easily incorporated in the microemulsions to give optically transparent solutions. The concentration of the substrate in the suspension was ca. 2.4×10^{-3} M. Irradiation of **1**–**3** incorporated in the microemulsions almost exclusively results in the formation of the h-h cyclomers (Table 1). The mass balance for this photocycloaddition was close to 100%. Furthermore, the quantum yields for the photocycloaddition in the microemulsions are remarkably greater than those in methylene chloride. For example, after 20 min of irradiation of the microemulsion sample, the conversion was ca. 80%. Under identical conditions a similar conversion for the sample in methylene chloride solution needs more than 1 h of irradiation. Fig. 1 shows the absorption spectra of **3** in the microemulsions as a function of irradiation time. Obviously, after 40 min irradiation, the conversion was close to 100%. The greater quantum yields for **1**–**3** photocycloaddition in microemulsions are evidently due to the higher local concentration. As described above, the substrate molecules bearing an ionic or a polar substituent should be concentrated at the interface of the water pool. Based on the AOT content and the molar ratio of water to AOT used in the microemulsion preparation, the concentration of the water pool is calculated to be ca. 4.7×10^{-4} M.[10] Thus, under the bulk concentration of the substrate used (2.4×10^{-3} M), each water pool contains 5.1 molecules of the substrate. In consideration of the small size of the water microdroplet, the local concentration of the substrate should be much higher than the bulk concentration. The almost exclusive formation of the h-h cyclomer is attributed to the preorientation of substrate molecules at the water pool interface. Because of the hydrophobicity of the anthracene moiety and the charged or polar nature of the substituent, the anthracene chromophore for **1**–**3** should reside in the organic phase, while the substituent is anchored among the surfactant headgroups at the water pool interface. Thus, the molecular plane would tend to be perpendicular to the interface of water pool, and the substituent is directed towards the water pool. Consequently, the photocycloadditon of two neighboring anthracene molecules favors the formation of h-h cyclomers. In contrast, the non-polar reference substrate **5** should be solublized in the organic phase and lacks such an enhancement of local concentration and

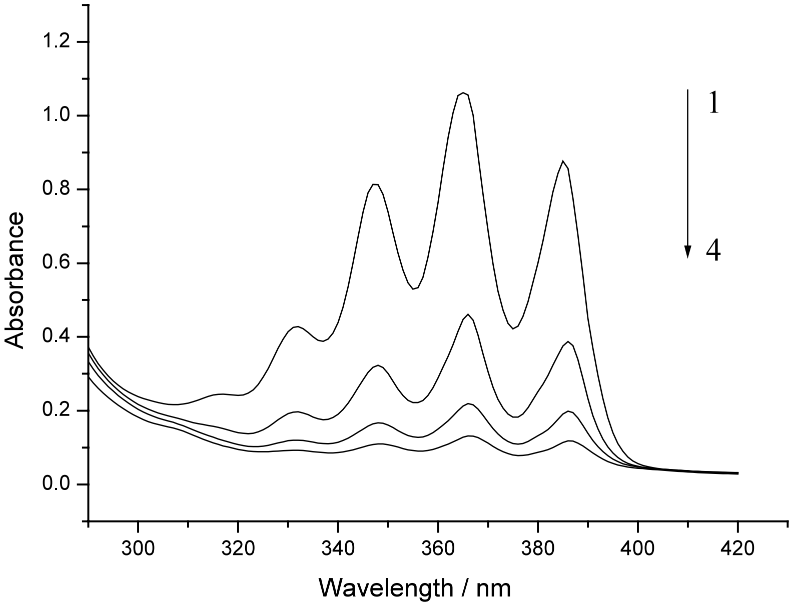

Figure 1. Absorption spectra of **3** in microemulsions as a function of irradiation time. 1, 0 min; 2, 15 min; 3, 30 min; 4, 60 min.

the preorientation in microemulsions. The product distribution (Table 1) and the quantum yield for the photocycloaddition are comparable with those in methylene chloride. For the less polar substrate **4**, only a fraction of its molecules is concentrated and preorientated at the interface of the water pool. As a result, the photocycloaddition quantum yield and the ratio of the h-h to h-t cyclomers (Table 1) were observed to be increased compared with those in methylene chloride, but the increased extent is not as large as those for **1**–**3**.

Acknowledgements

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