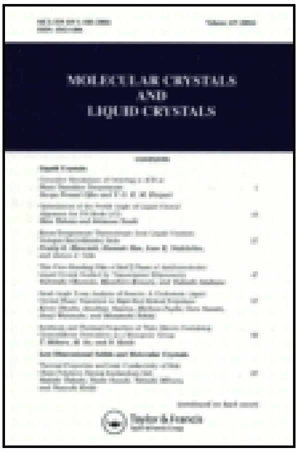

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Photochemical Cyclodimerization of Cinnmamic Acids Included in Surfactant Amine Oxides

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PHOTOCHEMICAL CYCLODIMERIZATION OF CINNMAMIC ACIDS INCLUDED IN SURFACTANT AMINE OXIDES

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Abstract Photocyclodimerization of unsubstituted and *p*-methoxy substituted cinnamic acids incorporated in micelles, vesicles or microemulsions formed by dodecyl-(C_{12}DAO) and hexadecyl-dimethylamine oxides (C_{16}DAO) has been studied in water. The dimerization proceeds in the vesicle much more efficiently than in the micelles with preferable formation of head-to-head dimers. The photoreactivity and the stereochemistry of cyclodimers are affected by structural change of the molecular aggregates.

INTRODUCTION

Photocyclodimerization of cinnamic acid is an excellent probe for a study of effect of molecular orientation imposed by organized reaction media.[1, 2, 3] Stereochemistry of cyclodimers in the photolysis of cinnamic acids exactly reflects the molecular alignment in their various crystal forms (morphorism).[4] Such a preorientation of guest molecules have been confirmed to be effective in layered inorganic minerals[5] as well as normal or inverse minerals.[6]

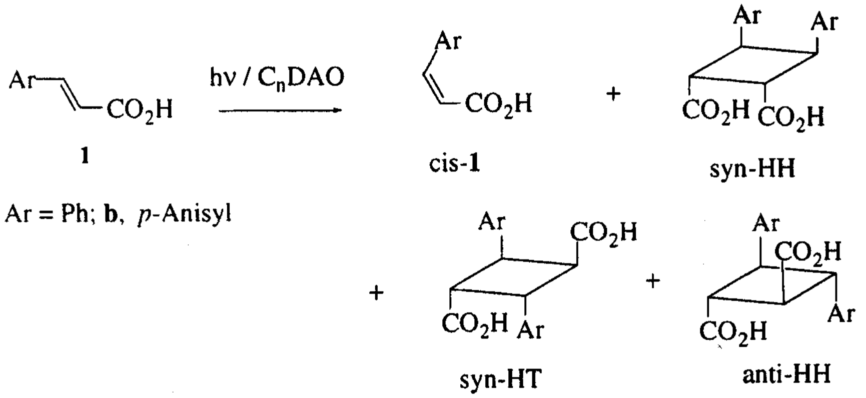
Surfactant dimethylamine oxides (C_nDAO, n = 12 -18 where n means alkyl carbon number) are known to form a number of aggregates in water depending on the concentrations and temperatures.[7] Thus, C_{16}DAO and C_{18}DAO exhibit iridescent colors in diluted aqueous solutions at surfactant concentrations of 0.3 - 2 wt %. This iridescence was explained by the interference of light arising from the Bragg refraction between multilamellar layers of vesicular aggregates. Such molecular aggregates change from micelle to vesicle in structure by the addition of cinnamic acid in various ratios against C_nDAO.[8]

In the present paper, the authors wish to report on the photocyclodimerization of unsubstituted and *p*-methoxy substituted cinnamic acids incorporated in the organized media of C_{12}DAO and C_{16}DAO in water.

RESULTS AND DISCUSSION

Photochemical Cyclodimerization of Cinnamic Acids in Aqueous C_nDAO Solution

Irradiation of a 5.0 mM cinnamic acids (**1a**, **b**) in 1.0 - 5.0 mM C_nDAO (n= 12 and 16) in water by UV light from a 300 W Hg lamp through a pyrex filter for 15 h gave rise to the cortresponding δ-truxinic (*anti*-HH), β-truxinic (*syn*-HH), α-truxillic acids (*syn*-HT), and *cis*-isomer in yields as shown in TABLE I. The cyclodimers were identified by HPLC, NMR, and MS spectroscopies in comparison with those of the authentic samples. Product isolation was done by a conventional SiO_2 column chromatography after separation of photoproducts from C_{16}DAO by acidification with 6N HCl followed by extraction with ethyl ether.



a, Ar = Ph; b, *p*-Anisyl

TABLE I Photocyclodimerization of cinnamic acids (**1a**, **b**) in aqueous C_nDAO[a]

Cinnamic acid (1)	C_nDAO[b] (n)	[1] [C_nDAO]	Aggregated form	Dimer yields (%)	Selectivity (%) *syn*-HH	*anti*-HH	*syn*-HT
1a (H)	12	0.2	spherical micelles	2.6	7	64	26
		0.6	vesicles	16.7	21	59	20
		1.0	vesicles	32.9	29	59	11
	16	0.2	rodlike micelles	2.5	19	83	0
		0.6	vesicles	17.4	23	63	16
		1.0	vesicles	29.9	28	59	14
1b (MeO)	12	0.2	spherical micelles	5.1	18	63	22
		0.6	vesicles	26.5	30	55	16
		1.0	vesicles	47.3	42	43	15

[a] Irradiation was carried out by means of a pyrex-filtered 300W Hg lamp at the concentrations of 5.0 mM substrate in the presence of C_nDAO. [b] C_{12}DAO: Dodecyldimethylamine oxide; C_{16}DAO: Hexadecyldimethylamine oxide.

Cyclodimerization occurred gradually after an attainment of a photostationary state (trans : cis = *ca.* 2.2) within 30 min. Control experiment indicates that observable reaction was only cis-trans isomerization in photolysis of sodium cinnamate in 5.0 mM aquous solution without C_nDAO. TABLE I shows the following characteristics. That is, an increase of the molar ratios of **1** against C_nDAO resulted in the change of molecular aggregates from micelles to vesicles. According to the structural change, the photodimerization not only improved in efficiency, but also changed in the distribution of isomeric cyclodimers. Vesicle favors the formation of *syn*-HH at the expence of *anti*-HH and *syn*-HT dimers. Stereoisomeric distribution tells us a head-to-head (HH) alignment of the starting **1** in the aggregate. Weak acids such as cinnamic acid bind electrostatically with weak base, C_nDAO, to form ion pairs, the anionic parts of which, in part, are located on the bilayer surface. While, some of the other anions are partly intercalated into bilayer by directing hydrophobic aromatic rings toward the interior of the bilayer. In such situation, HH and HT (head-to-tail) pairings are plausible, which, on irradiation, lead to HH and HT dimers, respectively. With an increase of the ratio of [**1**] to C_nDAO, the fraction of the intercalated cinnamic acids increases on account of its hydrophobicity. This is correlated with the fact that introduction of methoxy group into phenyl group makes cinnamic acid more hydrophobic and, therefore enhances the selectivity of *syn*-HH dimer in the three isomers. In addition, *anti*-HH is always formed in a higher yield than *syn*-HH.[9] It is rational that *anti*-HH dimer is ca. 2 kcal/mole thermodynamicaly more stable than *syn*-HH on the basis of theMM2 calculation.

Effect of pH on Photodimerization of Cinnamic Acid in Aqueous C_{16}DAO Solution

The total yield of all the isomeric dimers from photolysis of an equimolar mixture of **1a** and C_{16}DAO in water (5.0 mM) was maximum at pH of around 4, below or above which

TABLE II Effect of pH on chemical yields for photocyclodimerization of cinnamic acid (**1a**) in C_{16}DAO and their aggregated forms[a]

pH[b]	conv. (%)	Selectivity of products (%)			*syn*-HH / *anti*-HH	Aggregated form
		cis-**1a**	Dimers	(*syn*-HH : *anti*-HH)[c]		
1.6	72	68	32	(46 : 50)	0.92	micro emulsion
2.6	79	49	51	(42 : 58)	0.72	
3.8	83	42	58	(24 : 58)	0.41	vesicles
5.0	73	73	27	(29 : 71)	0.41	
5.5	80	95	5	(– : –)	–	rodlike micelles

[a] Irradiation was carried out by means of a pyrex-filtered 300W Hg lamp for 7 h at the concentrations of 5.0 mM substrate. [b] Adjustment of pH of the solutions were done by adding 5.0 mM HCl or NaOH. [c] Figures in parentheses are dimer distributions.

they decrease as shown in TABLE II.

The photoreactivities improved significantly from micelles (pH 5) to vesicles (pH ca. 4). The ratio of *syn*-HH to *anti*-HH decreases with lowering pH. The results are coincident with the structural change of the molecular aggregate due to destruction of the 1:1 ion pairing between cinnamic acid and the surfactant amine oxide by the addition of HCl.

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