

MICELLAR ALIGNMENT EFFECT ON THE PHOTODIMERIZATION OF 2-PYRIDONES

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We have previously showed that photochemical reactions ¹⁾ in the micellar systems gave the products in good yield due to the condensation effect of micelle on the substrate. We will report a micellar alignment effect on the photodimerizations of 2-pyridones (1 a-i), as an amphiphilic substrate, in the micellar systems.

The photoreaction of (1a) in water gave four [4+4]dimers (3a)-(6a), and an isomer (2a). The structures of the new products (4a), (5a), (6a), were established by means of the spectrometric data and chemical evidences. The other experimental results gave in Table. The reactions gave the following results : (i) in the case of (1 b-e), the C/T ratios of the dimers in the micellar system increased with decreasing concentration of substrate although the trans dimers were major product (60-80%), while the ratios in water or ethanol were independent ; (ii) in the case of (1 f-h), the yield of cis dimers increased up to 50% and with decreasing length of the carbon chain in the CTAB micelle ; (iii) in the case of (1i), the only cis dimers yielded at low concentrations (<15mM) in the CTAB micelle, while the trans dimers were major products (60-100%) in water or ethanol ; (iv) the increase of the cis dimers in micellar systems may be due to the alignment effect of micelle on the substrate.

In conclusion, the photodimerization of the amphiphilic substrate, which is difficult to dissolve in water, such as (1 c-e), is possible in aqueous media by using the solubilisation effect of micelle, and the control of the reaction, due to the alignment effect of micelle on the substrate, should be possible.

			sol. conc. cis:trans		sol. conc. cis:trans
			170 (mM) 35:65		EtOH 22 (mM) 15:85
(1)	(3)	(4)	H ₂ O 100 35:65	(1f)	7 0:100
	trans-anti	trans-syn	33 35:65	H ₂ O 22 21:79	
			S.L. 100 35:65	CTAB 22 50:50	
			33 36:64	7 49:51	
			170 21:79	EtOH 22 19:81	
			(1d) S.L. 60 33:67	7 0:100	
			33 35:65	(1h) H ₂ O 22 34:66	
			170 27:73	7 17:83	
			EtOH 100 28:72	CTAB 22 30:70	
			33 28:72	7 9:91	
			(1e) 170 33:67	EtOH 100 0:100	
			S.L. 100 36:64	22 *	
			33 38:62	(1i) H ₂ O 22 29:71	
			S.L.: 3% aq. Sodium laurate.	7 0:100	
			CTAB: 3.65% aq. Cetyl trimethyl ammonium bromide.	22 86:14	
			* The only isomer was yielded.	CTAB 15 100:0	
				7 100:0	

a: R' = CH ₃ R'' = H	f: R' = -(CH ₂) ₂ COOH R'' = H
b: R' = C ₄ H ₉ R'' = H	g: R' = -(CH ₂) ₅ COOH R'' = H
c: R' = C ₆ H ₁₃ R'' = H	h: R' = -(CH ₂) ₁₀ COOH R'' = H
d: R' = C ₈ H ₁₇ R'' = H	i: R' = -(CH ₂) ₂ COOH R'' = C ₃ H ₇
e: R' = C ₁₂ H ₂₅ R'' = H	

1) Y. Nakamura, et al., JCS. Chem. Comm., 1977, 887.
Y. Nakamura, et al., Chem. Lett., 1978, 965.