MICELLAR ALIGNMENT EFFECT ON THE PHOTODIMERIZATION OF 2-PYRIDONES

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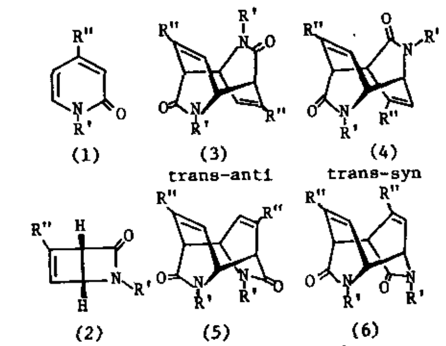
We have previously showed that photochemical reactions [1] in the micellar systems gave the products in good yeild due to the condensation effect of micelle on the substrate. We will report a micellar alignment effect on the photodimerizations of 2-pyridones (1 a-i), as an amphiphilic substrate, in the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



(1) (3) trans-anti (4) trans-syn (2) isomer (5) cis-anti (6) cis-syn

a: $R'=CH_3$ $R''=H$ f: $R'=-(CH_2)_2COOH$ $R''=H$
b: $R'=C_4H_9$ $R''=H$ g: $R'=-(CH_2)_5COOH$ $R''=H$
c: $R'=C_6H_{13}$ $R''=H$ h: $R'=-(CH_2)_{10}COOH$ $R''=H$
d: $R'=C_8H_{17}$ $R''=H$ i: $R'=-(CH_2)_2COOH$ $R''=C_3H_7$
e: $R'=C_{12}H_{25}$ $R''=H$

	solv.	conc.	cis:trans
(1b)	H_2O	170(mM)	35:65
		100	35:65
		33	35:65
	S.L.	170	32:68
		100	35:65
		33	36:64
(1d)	S.L.	170	21:79
		60	33:67
		33	35:65
(1e)	EtOH	170	27:73
		100	28:72
		33	28:72
	S.L.	170	33:67
		100	36:64
		33	38:62
(1f)	EtOH	22(mM)	15:85
		7	0:100
	H_2O	22	21:79
		7	16:84
	CTAB	22	50:50
		7	49:51
(1h)	EtOH	22	19:81
		7	0:100
	H_2O	22	34:66
		7	17:83
	CTAB	22	30:70
		7	9:91
(1i)	EtOH	100	0:100
		22 *	—
	H_2O	22	29:71
		7	0:100
	CTAB	22	86:14
		15	100:0
		7	100:0

S.L.:3%aq. Sodium laurate.
CTAB:3.65%aq. Cetyl trimethyl ammonium bromide.
* The only isomer was yeilded.

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