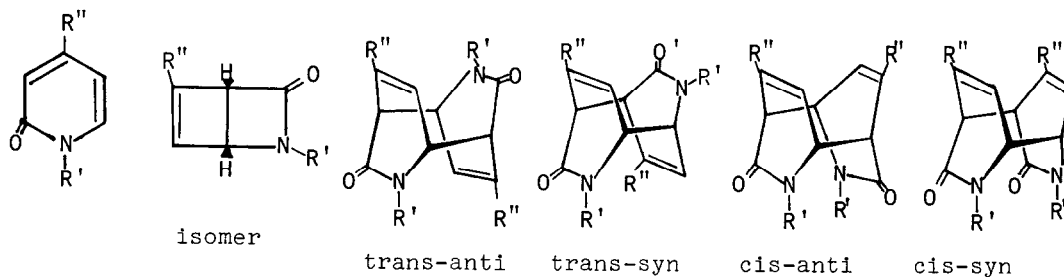


A MICELLAR ALIGNMENT EFFECT IN THE PHOTODIMERIZATIONS OF N- $\omega$ -CARBOXYALKYL-2-PYRIDONES AND THEIR 4-ALKYL DERIVATIVES IN MICELLE OR REVERSED MICELLE

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The photoreaction of N- $\omega$ -carboxyalkyl-2-pyridones at 7.2-22.4mM concentrations in micellar and reversed micellar systems gave the ratio of cis to trans dimer increasing with decreasing length of the alkyl chain and in their 4-alkyl derivatives, only cis dimer was obtained.

In the course of our biomimetic investigation utilizing "reaction in micelle,"<sup>1)</sup> we have previously showed that photochemical reactions in micellar system<sup>2)</sup> gave the products in good yields due to the condensation effect of the micelle on the substrate. In this communication, we will report a micellar alignment effect on the photodimerization of N- $\omega$ -carboxyalkyl-2-pyridones, used as an amphiphilic substrate, in micelle and reversed micelle. The 4+4 dimers formed in the photoreaction of N-methyl-2-pyridone in water have been unambiguously characterized by our recent work<sup>3)</sup> and their spectrometric data have enabled us to analyze the dimerization products of N- $\omega$ -carboxyalkyl-2-pyridones in micellar and other solvent systems.



I : R' = -(CH<sub>2</sub>)<sub>2</sub>COOH, R'' = H  
 II : R' = -(CH<sub>2</sub>)<sub>5</sub>COOH, R'' = H  
 III : R' = -(CH<sub>2</sub>)<sub>10</sub>COOH, R'' = H

IV : R' = -(CH<sub>2</sub>)<sub>2</sub>COOH, R'' = -C<sub>3</sub>H<sub>7</sub>  
 V : R' = -(CH<sub>2</sub>)<sub>2</sub>COOH, R'' = -C<sub>7</sub>H<sub>15</sub>

Table 1. Product distribution in the photoreaction of the pyridones(I-III)<sup>a)</sup>

Run	Comp. <sup>b)</sup>	Solvent	Conc. (mM)	Recovered starting comp.(%)	Yield <sup>c)</sup> of dimers	Proportion of dimers				Ratio of cis : trans
						t-a	t-s	c-a	c-s	
1	I	EtOH	100.0	20	37	75	0	25	0	25 : 75
2			22.4	0	41	85	0	15	0	15 : 85
3			7.2	0	7	100	0	0	0	0 : 100
4		H <sub>2</sub> O	100.0	6	56	71	2	13	14	27 : 73
5			22.4	17	39	79	0	8	13	21 : 79
6			7.2	8	16	84	0	0	16	16 : 84
7		CTAB	22.4	7	26	50	0	27	23	50 : 50
8			7.2	0	8	51	0	23	26	49 : 51
9		R.M. <sup>d)</sup>	22.4	4	45	58	2	16	24	40 : 60
10			7.2	0	33	53	0	21	26	47 : 53
11	II	CTAB	22.4	0	26	62	0	25	13	38 : 62
12			7.2	0	19	65	0	21	14	35 : 65
13		R.M.	22.4	13	44	56	11	15	18	33 : 67
14			7.2	0	27	58	0	18	24	35 : 65
15	III	EtOH	100.0	19	36	81	0	19	0	19 : 81
16			22.4	0	17	81	0	19	0	19 : 81
17			7.2	10	5	100	0	0	0	0 : 100
18		H <sub>2</sub> O <sup>e)</sup>	100.0	0	38	62	0	22	16	38 : 62
19			22.4	0	45	66	0	18	16	34 : 66
20			7.2	0	15	83	0	0	17	17 : 83
21		CTAB	22.4	0	38	70	0	15	15	30 : 70
22			7.2	10	15	91	0	0	9	9 : 91
23		R.M.	22.4	10	50	77	0	23	0	23 : 77
24			7.2	3	28	85	0	15	0	15 : 85

a) All new products gave satisfactory elemental analyses.

b) The solubilities of I, II and III in water are  $2.5 \times 10^{-1} \text{M}$ ,  $2.3 \times 10^{-1} \text{M}$  and  $7.2 \times 10^{-5} \text{M}$ , respectively.

c) The yield is percentage based on the recovered starting compound and the other product was only isomer.

d) R.M. = reversed micellar system

e) Used as the sodium salts on account of slightly soluble in water.

The photoreactions were carried out as follows; solutions of the pyridones (I-V) in 0.1M aq. cetyltrimethylammonium bromide(CTAB), 0.12M dodecylammonium acetate-0.12M dodecylamine-0.69M water-cyclohexane(as reversed micellar system), abs. EtOH, or in water were irradiated by 400W high pressure mercury arc lamp in Pyrex cell with a fine stream of N<sub>2</sub> bubbles at 25° C for 15h. The reaction mixtures were separated by means of ion-exchange and/or silica-gel thin layer chromatography. The product distributions at different concentrations of the substrates in the micellar, reversed micellar and other solvent systems are shown in Table 1 and 2.

Table 2. Product distribution in the reaction of the pyridones(IV and V)<sup>a)</sup>

Run	Comp. <sup>f)</sup>	Solvent	Conc. (mM)	Recovered starting comp.(%)	Yield <sup>c)</sup> of dimers	Proportion of dimers				Ratio of cis : trans
						t-a	t-s	c-a	c-s	
25	IV	EtOH	100.0	41	12	100	0	0	0	0 : 100
26			22.4	0	0	0	0	0	0	— <sup>g)</sup>
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27		H <sub>2</sub> O	500.0 <sup>e)</sup>	23	71	46	14	28	12	40 : 60
28			22.4 <sup>e)</sup>	2	16	48	24	14	14	28 : 72
29			7.2	4	3	79	21	0	0	0 : 100
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30		CTAB	22.4	5	29	14	0	49	37	86 : 14
31			15.0	16	17	0	0	65	35	100 : 0
32			7.2	0	13	0	0	44	56	100 : 0
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33		R.M. <sup>d)</sup>	22.4	4	22	21	0	51	28	79 : 21
34			15.0	4	12	0	0	50	50	100 : 0
35			7.2	0	25	0	0	64	36	100 : 0
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36	V	EtOH	100.0	34	0	0	0	0	0	— <sup>g)</sup>
37		H <sub>2</sub> O	22.4 <sup>e)</sup>	3	21	43	16	26	15	41 : 59
38		CTAB	22.4	0	12	0	0	61	39	100 : 0

a), c), d), e) See the Table 1.

f) The solubilities of IV and V in water are  $7.8 \times 10^{-3} \text{M}$  and  $4.0 \times 10^{-5} \text{M}$ , respectively.

g) Only isomer was obtained.

In the photoreaction of the pyridones(I-V) in water and EtOH under these conditions, the cis/trans ratios of the dimers were independent of the alkyl chain length(compare, for instance, run 3, 6, 17 and 20 in the Table 1) and the proportion of the trans dimers was very high(59-100%). The reaction in the anhydrous solvent gave only anti dimers and in aqueous solvent, syn dimer was additionally obtained. In contrast, the cis/trans ratios in the reaction of I-III in the micellar and reversed micellar systems increased up to 1.0(run 7) and with the decrease of the alkyl chain length(compare, run 8, 10, 12, 14, 22 and 24 in the Table 1). The effect of the micelle was even more dramatic for the 4-propyl and 4-heptyl pyridones(IV and V). In fact, the ratio was strongly reversed and the efficiency was greatly increased in the both micellar systems (compare, run 29, 32, 35, 37 and 38 in the Table 2). The above results suggest that not only the distribution of the solubilizates between micellar and bulk phases(water or cyclohexane) but also the site of incorporation of the pyridone moiety<sup>4)</sup> may play important roles to give stereospecifically the cis dimer.

In conclusion, the photodimerization of the amphiphilic substrate is possible in micellar<sup>5)</sup> and reversed micellar<sup>6)</sup> systems and the control of the reaction should be possible. The mechanistic study is now under way.

#### References and Notes

- 1) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems." Academic Press, 1975.
- 2) Y. Nakamura, Y. Imakura, T. Kato, and Y. Morita, J. Chem. Soc., Chem. Commun., 1977, 887; Y. Nakamura, Y. Imakura, and Y. Morita, Chem. Lett., 1978, 965.
- 3) Y. Nakamura, T. Kato, and Y. Morita, J. Chem. Soc., Chem. Commun., 1978, 620.
- 4) Especially, see the remarkable differences between the cis/trans ratios in the reactions of III and V which should be almost incorporated in the micellar phase in order to insoluble in water; see run 21, 22 and 38 and notes in the Tables
- 5) The first micellar effect in the photodimerization in micellar system have been reported by P. de Mayo<sup>7)</sup> and our group.<sup>8)</sup>
- 6) This communication may be a first report in the photodimerization in reversed micellar system.
- 7) K-H. Lee and P. de Mayo, J. Chem. Soc., Chem. Commun., 1979, 493.
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