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Reactions Using Micellar Systems. IV.[1] Regioselectivity in the Photodimerizations of 2-Pyridones in Micelles and Reversed Micelles

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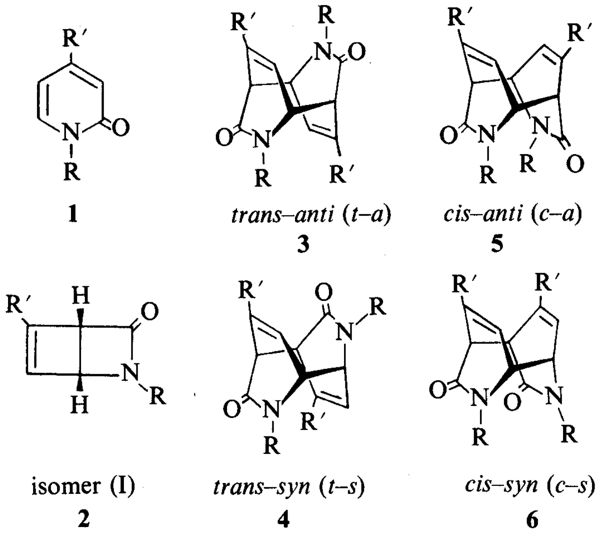
Photodimerizations of *N*-alkyl-2-pyridones (**1a**—**e**), *N*-ω-carboxyalkyl-2-pyridones (**1f**—**h**), and *N*-2′-carboxyethyl-4-alkyl-2-pyridones (**1i** and **1j**) in micellar and reversed micellar systems gave the following results; 1) in the reactions of **1a**—**e**, the *cis*/*trans* ratios of dimers increased with decreasing concentration of the probes, with the octyl compound (**1d**) showing the highest selectivity; 2) in the case of **1f**—**h**, the ratios increased up to 1.0 with decreasing alkyl chain length; 3) below 7.2 mM concentration, **1i** gave exclusively the *cis* dimer, while only the *trans* dimer was formed when the reaction was carried out in water. The results indicate that the regio-control of the reactions was a result of the alignment effect of micelles on the substrate, and moreover, in both micellar systems, not only the distribution of amphiphilic probes between micellar and bulk (water or cyclohexane) phases but also the orientation and incorporation site of the pyridone moiety play important roles in the regioselectively for the *cis* dimer.

Keywords——*N*-alkyl-2-pyridone; *N*-ω-carboxyalkyl-2-pyridone; *N*-2′-carboxyethyl-4-alkyl-2-pyridone; micelle; reversed micelle; [4+4] dimer; photodimerization; regioselectivity; alignment effect; amphiphile

Various reactions related to organic and biomimetic chemistry have been studied extensively in micellar systems,[2] but the reaction sites, *e.g.*, in micelle-catalyzed hydrolysis,[3] have been mostly on the surface of micelles. Furthermore, photoreactions in micellar systems have not given satisfactory results.[4] We therefore investigated a photo-induced reaction (photodimerization) in micellar systems, with special emphasis on reaction in the hydrophobic portions of micelles, and reported the successful photodimerization of acenaphthylene as a hydrophobic substrate in micellar systems.[5] Since then, many photochemical reactions in micellar systems have been investigated, such as photo-induced hydrogen abstraction,[6] fragmentation,[7] and cycloaddition reactions.[8]

On the other hand, very little work has been done on the reactions in reversed micellar systems[9] compared with those in (normal) micellar systems, and nothing is known of photochemical reactions in such a system.

Our first report of the photodimerization of acenaphthylene in a micellar system[5] indicates that the reaction of a hydrophobic substrate is possible in aqueous media by using the solubilization and condensation effects of micelles on the substrate. In order to study the regio-control of reactions in micellar systems we investigated and preliminarily reported[1] the photochemical dimerizations of 2-pyridones (which, in water, gave the four [4+4] dimers shown in Chart 1[10]) in micellar and reversed micellar systems. We now describe in detail the regio-controlled photodimerizations of *N*-alkyl-2-pyridones (**1a**—**e**), and *N*-ω-carboxyalkyl-2-pyridones and their 4-alkyl derivatives (**1f**—**j**) in micellar and reversed micellar systems.



a: $R=CH_3$, $R'=H$
b: $R=C_4H_9$, $R'=H$
c: $R=C_6H_{13}$, $R'=H$
d: $R=C_8H_{17}$, $R'=H$
e: $R=C_{12}H_{25}$, $R'=H$
f: $R=-(CH_2)_2COOH$, $R'=H$
g: $R=-(CH_2)_5COOH$, $R'=H$
h: $R=-(CH_2)_{10}COOH$, $R'=H$
i: $R=-(CH_2)_2COOH$, $R'=C_3H_7$
j: $R=-(CH_2)_2COOH$, $R'=C_7H_{15}$

Chart 1

Experimental Procedure and Results

Photoreactions of *N*-Alkyl-2-pyridones (1a—e) in Micellar and Homogeneous Solvent Systems

The general experimental procedure was as follows; a solution of the pyridone (**1**) in 3% aq. sodium laurate (SL micelles), water, abs. ethanol (EtOH) or benzene was irradiated with a 400 W high-pressure mercury arc lamp in a Pyrex cell at 25 °C for 15 h while a fine stream of nitrogen bubbles was passed through the solution. The solvent was evaporated off *in vacuo*, then the residue was separated by silica gel thin-layer chromatography (TLC). The resulting products were an isomer (**2**) and the *trans–anti* (**3**), *trans–syn* (**4**), *cis–anti* (**5**), and *cis–syn* (**6**) dimers, and their distributions at different concentrations of substrates in the micellar and other solvent systems are shown in Table I.

In the photoreactions of the pyridones (**1a**—**e**) in water, EtOH or benzene under these conditions, the ratios of dimers to the isomer (**2**) increased with increasing concentration of substrate, but those of *cis/trans* dimers were independent of the concentration of substrate. The reactions in anhydrous EtOH or benzene gave only *anti* dimers, whereas in aqueous solvent *syn* dimers were also obtained.[11] In contrast, the *cis/trans* ratios of dimers in the reactions in SL micelles increased with decreasing concentration of substrate, and the enhancements apparently decreased in the following order of alkyl chain length; octyl > hexyl > dodecyl > butyl > methyl.

These results indicate that regio-controlled photodimerization should be possible by the use of a micellar system, though the proportions of *trans* dimers are still very high (>60%).

Photoreactions of *N*-ω-Carboxyalkyl-2-pyridones (1f—h) in Micellar and Homogeneous Solvent Systems

To provide much more effective folding of the detergent and preferential ordering of pyridone probes in the micelles, photoreactions of the carboxyalkyl pyridones (**1f**—**h**) were

TABLE I. Photoreactions of *N*-Alkyl-2-pyridones (**1a**—**e**) in Micellar and Homogeneous Solvent Systems

Comp.[e]	Medium	Conc. (mM)	Conversion[a] (%)	Yield[b] of dimer (%)	Ratio[c] of *D*/*I*	Distribution of dimer				Ratio[d] of *C*:*T*
						t–a	*t–s*	*c–a*	*c–s*	
1a	H_2O	170	94	84	6.6	67	1	22	10	32:68
		100	97	61	3.5	65	2	22	11	33:67
		30	95	52	1.6	62	3	22	13	35:65
	EtOH	170	62	85	5.8	56	0	44	0	44:56
		30	66	62	1.6	64	0	36	0	36:64
	Benzene	170	82	88	7.2	60	0	40	0	40:60
		100	85	58	4.5	61	0	39	0	39:61
	SL	170	88	68	8.1	62	2	24	12	36:64
		100	91	77	5.9	63	2	22	13	35:65
		30	100	43	1.3	59	3	25	13	38:62
1b	H_2O	170	93	76	4.2	61	4	19	16	35:65
		100	100	74	3.9	60	4	19	17	36:64
		30	100	51	1.2	62	3	18	17	35:65
	SL	170	100	70	4.1	63	5	16	16	32:68
		100	100	67	2.8	61	4	14	21	35:65
		30	87	51	1.6	59	4	15	22	37:63
1c	SL	170	90	70	5.4	75	3	8	14	22:78
		100	100	67	4.8	66	6	9	19	28:72
		30	100	51	1.1	60	8	6	26	32:68
1d	SL	170	90	68	5.2	75	4	7	14	21:79
		100	95	53	1.6	61	6	9	24	33:67
		30	100	43	0.9	58	7	8	27	35:65
1e	EtOH	170	99	30	1.3	73	0	27	0	27:73
		100	87	23	0.7	72	0	28	0	28:72
		30	92	23	0.4	72	0	28	0	28:72
	Benzene	100	96	24	0.9	73	0	27	0	27:73
		30	100	16	0.3	75	0	25	0	25:75
	SL	170	87	59	2.7	59	8	16	17	33:67
		100	93	38	1.3	58	6	13	23	36:64
		60	98	42	0.9	53	8	9	30	39:61
		30	100	25	0.6	55	6	4	35	39:61

a) Based on the recovered starting compound.
b) Based on the conversion.
c) The ratio of dimers (*D*) to isomer (*I*) isolated.
d) The ratio of *cis* dimer (*C*) to *trans* dimer (*T*).
e) Solubility in water (or SL micelles); **1a** and **1b**, soluble; **1c**, 2.8×10^{-2} (3.2×10^{-1}); **1d**, 3.0×10^{-3} (2.2×10^{-1}); **1e**, 3.8×10^{-5} (1.7×10^{-1}).

carried out under the same conditions as described above except for the use of a micellar system which consisted of 0.1 M aq. cetyltrimethylammonium bromide (CTAB micelles). The experimental results are shown in Table II.

In the photoreactions of **1f**—**h** in homogeneous solvents under these conditions, the *cis*/*trans* ratios of dimers were independent of the alkyl chain length, *e.g.*, at 7.2 mM the ratios in the reactions of **1f** and **1h** in water were 0.19 and 0.20, respectively, and in EtOH only *trans–anti* dimers were obtained. Interestingly, in the photoreactions in CTAB micelles, the *cis*/*trans* ratios of dimers increased up to 1.0 with decreasing alkyl chain length, *i.e.*, at 7.2 mM, the ratios in the cases of **1f**, **1g**, and **1h** were 0.96, 0.54, and 0.10, respectively.

Table II. Photoreactions of *N*-ω-Carboxyalkyl-2-pyridones (**1f**—**h**) in Micellar and Homogeneous Solvents Systems

Comp.[f]	Medium	Conc.[h] (mM)	Conversion[a] (%)	Yield[b] of dimer (%)	Distribution of dimer				Ratio[d] of $C:T$
					t–a	*t–s*	*c–a*	*c–s*	
1f	H_2O	100.0	94	56	71	2	13	14	27:73
		22.4	83	39	79	0	8	13	21:79
		7.2	92	16	84	0	0	16	16:84
	EtOH	100.0	80	37	75	0	25	0	25:75
		22.4	100	41	85	0	15	0	15:85
		7.2	100	7	100	0	0	0	0:100
	CTAB	22.4	93	26	50	0	27	23	50:50
		7.2	100	16	51	0	23	26	49:51
1g	CTAB	22.4	100	26	62	0	25	13	38:62
		7.2	100	19	65	0	21	14	35:65
1h	H_2O[g]	100.0	100	38	62	0	22	16	38:62
		22.4	100	45	66	0	18	16	34:66
		7.2	100	15	83	0	0	17	17:83
	EtOH	100.0	81	36	81	0	19	0	19:81
		22.4	100	17	81	0	19	0	19:81
		7.2	90	5	100	0	0	0	0:100
	CTAB	22.4	100	38	70	0	15	15	30:70
		7.2	90	15	91	0	0	9	9:91

a)—*d*) See the references in Table I.
f) Solubility in water: **1f**, 2.5×10^{-1} M; **1g**, 2.3×10^{-1} M; **1h**, 7.2×10^{-5} M.
g) By use of the sodium salt of **1h** because of insolubility in water.
h) Volumes of 20, 50, and 200 ml were used at the concentrations of 100.0, 22.4, and 7.2 mM, respectively.

Table III. Photoreactions of *N*-2′-Carboxyethyl-4-alkyl-2-pyridones (**1i**) and (**1j**) in Micellar and Homogeneous Solvents Systems

Comp.[i]	Medium	Conc.[h] (mM)	Conversion[a] (%)	Yield[b] of dimer (%)	Distribution of dimer				Ratio[d] of $C:T$
					t–a	*t–s*	*c–a*	*c–s*	
1i	H_2O	500.0[g]	77	71	46	14	28	12	40: 60
		22.4[g]	98	16	48	24	14	14	28: 72
		7.2	96	3	79	21	0	0	0:100
	EtOH	100.0	59	12	100	0	0	0	0:100
		22.4	100	0	0	0	0	0	—[j]
	CTAB	22.4	95	29	14	0	49	37	86: 14
		15.0	84	17	0	0	65	35	100: 0
		7.2	100	13	0	0	44	56	100: 0
1j	H_2O	22.4[g]	97	21	43	16	26	15	41: 59
	EtOH	100.0	66	0	0	0	0	0	—[j]
	CTAB	22.4	100	12	0	0	61	39	100: 0

a)—*g*) See the references in Table II.
i) Solubility in water: **1i**, 7.8×10^{-3} M; **1j**, 4.0×10^{-5} M.
j) Only the isomer was obtained.

This study indicates that the carboxy group and polymethylene chain length of substrates play an important role in the alignment effect of micelles, with the pyridone having the shortest polymethylene chain (**1f**) showing the highest selectivity, though the proportion of *trans* dimers was still high (>50%) due to the high solubility in water (2.5×10^{-1} M). In accordance with this explanation, the reaction of **1f** in bulk water gives predominantly *trans* dimers. These results suggest that high hydrophobicity of the pyridone moiety of **1f** is important for its incorporation into the micellar core, so that the proportion of *cis* dimer becomes much higher.

Photoreactions of *N*-2′-Carboxyethyl-4-alkyl-2-pyridones (1i) and (1j) in CTAB Micellar and Homogeneous Solvent Systems

In order to obtain supporting evidence for the above suggestion, pyridones (**1i** and **1j**) having a propyl or heptyl group at the 4-position were synthesized and irradiated under the same conditions as described above. Table III summarizes these results.

In homogeneous solvents, the photoreactions of **1i** and **1j** gave dimers in low yields compared with those of **1f**—**h** because of steric factors; in the case of **1i** in water, only the *trans* dimer was obtained at 7.2 mM and in EtOH no dimer was observed at 22.4 mM. In contrast, the reactions in CTAB micelles gave very different results. In particular, the *cis* dimer was exclusively obtained below 15.0 mM **1i** and 22.4 mM **1j**.

It should be noted that the remarkable differences between the *cis*/*trans* ratios in the photoreactions of **1h** and **1j** in micelles were observed in spite of the fact that both of them should be largely incorporated in the micellar core because of their similar insolubilities in water (see the references in Tables II and III).

Photoreactions of 1f—1j in Reversed Micellar System

The irradiations were carried out under the same conditions as described above except for the use of a reversed micellar system composed of 0.12 M dodecylammonium acetate, 0.12 M dodecylamine and 0.69 M water in cyclohexane. The purpose of the reversed micellar system is to hold the anionic probes in the reversed micellar surface. Table IV shows the experimental results.

Surprisingly, the photoreactions in the reversed micellar system gave results very similar to those in the CTAB micellar system as regards the *cis*/*trans* ratios of dimers. Thus, the pyridone with the shortest polymethylene chain (**1f**) shows the highest selectivity. In the case

TABLE IV. Photoreactions of **1f**—**i** in Reversed Micellar System

Comp.	Medium	Conc. (mM)	Conversion[a] (%)	Yield[b] of dimer (%)	Distribution of dimer				Ratio[d] of $C:T$
					t–a	*t–s*	*c–a*	*c–s*	
1f	RM[k]	22.4	96	45	58	2	16	24	40:60
		7.2	100	33	53	0	21	26	47:53
1g	RM	22.4	87	44	56	11	15	18	33:67
		7.2	100	27	58	0	18	24	42:58
1h	RM	22.4[l]	90	50	77	0	23	0	23:77
		7.2	97	28	85	0	15	0	15:85
1i	RM	22.4	96	22	21	0	51	28	79:21
		15.0	96	12	0	0	50	50	100: 0
		7.2	100	7	0	0	64	36	100: 0
1j	RM	22.4	100	15	0	0	62	38	100: 0

a)—*d*) See the references in Table I.
k) Reversed micelles.
l) Saturated solution.

of **1h**, the ratio of *cis–anti* to *cis–syn* dimer contrasts sharply with that found for the reaction in the CTAB micellar system.

Discussion

Menger[12)] reported that in dodecyltrimethylammonium ion micelles, highly water-insoluble guest molecules such as benzene, steroids and pyrene are solubilized in the grooves near the micellar surface, *i.e.*, in the Stern region,[13)] and water penetrates the micelles up to at least the first 6 of the 12 tail carbons.

On the basis of Menger's model, it can be considered that 1) the pyridone moieties of alkyl probes (**1a**—**e**) in SL micelles are incorporated in the Stern region, whereas the polymethylene chains are held in the hydrophobic core; 2) in the cases of **1f**—**j**, the carboxy groups in CTAB micelles hold together the head groups of detergents on the micellar surface by electrostatic interaction while the pyridone moieties may be incorporated in the grooves near the micellar surface, but not in the recesses of the micelles due to the hydrophilic character. Chart 2 shows that molecules having a longer polymethylene chain such as **1h** must be bent such that the end pyridone moiety lies near the micellar surface, while those having a short chain such as **1f**, **1i**, or **1j** could not be greatly bent because of the intramolecular steric and/or dipole-dipole interactions, but the pyridone moiety still lies in the Stern region. Furthermore, the 4-alkyl chains of **1i** and **1j** strongly interact with the polymethylene chains of detergents by hydrophobic forces, so that these chains are tightly aligned in the micelles. This interpretation is supported by the following evidence, reported by Whitten;[6a)] photo-induced hydrogen abstraction of 16-oxo-16-(*p*-tolyl)hexadecanoic acid in micelles yields only 4-methylacetophenone with a high quantum yield (0.8), indicating that the polymethylene chain is mostly bent such that both ends lie near the micellar surface.

According to the above considerations, our experimental results in micellar systems can be interpreted as implying that 1) in the reactions of *N*-alkyl pyridones (**1a**—**e**), the concentration dependences of *cis*/*trans* ratios, with the octyl compound (**1d**) showing the highest selectivity, and the high proportion of *cis–syn* dimer at low concentration occur due to the alignment effect of micelles on the substrate, while the pyridone moieties lie in the Stern region; 2) since all of the carboxy pyridones (**1f**—**j**) on photodimerization in CTAB micelles give *cis–syn* dimer as a common product, the pyridone moieties lie in the Stern region whether the molecules are bent (**1g** or **1h**) or not (**1f**, **1i**, or **1j**), or in the bulk water phase; 3) since the highest selectivity is observed in the reaction of **1f**, having the shortest polymethylene chain, in micelles, while the reaction of **1h**, having a longer chain, gives a product distribution very similar to that in water, the pyridone moiety of **1h** is incorporated with freely bent in Stern region, which contains water molecules, whereas that of **1f** is much more tightly aligned in the Stern region; 4) since completely reversed *cis*/*trans* ratios of dimers in the reactions in micelles and water were observed, especially at 7.2 mM **1i** and 22.4 mM **1j**, with higher selectivity of **1j** than **1i**, the molecules must be tightly aligned without bending in the micelles, and **1j**, having the longer chain at the 4-position, should be more strongly held than **1i** by hydrophobic interactions.

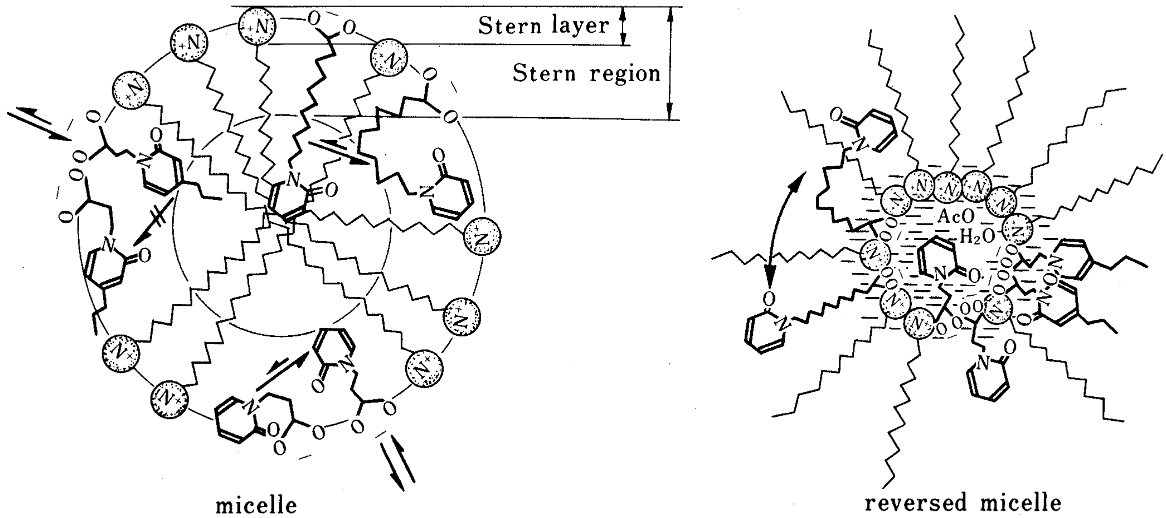
On the other hand, micellar structures in nonpolar solvents are generally the inverse of those formed in water, so-called "reversed or inverted micelles."[2)] Wong[14)] reported that sodium di-2-ethylhexyl sulfosuccinate in heptane forms reversed micelles having the ability to solubilize large amounts of water confined in spherical pools; the water molecules are only in contact with the polar head groups, and do not penetrate the micelle hydrophobic phase. Fendler[15)] also reported the formation and structure of reversed micelles of alkylammonium carboxylate in various nonpolar solvents.

As detergents forming reversed micelles, we used dodecylammonium acetate and dodecylamine, the latter amine does not behave itself as detergent but does so when it is complexed with substrates having a carboxy group by electrostatic interaction, *i.e.*, as dodecylammonium carboxylate. The carboxy groups of **1f**—**j** in the reversed micellar system hold the amino group of the detergent on the surface, while the site of incorporation of the pyridone moiety depends on the polymethylene chain length and the distribution of the molecule between the water pool and the hydrophobic bulk phase, *i.e.*, **1f** and **1g** having relatively high solubility in water (see the references in Tables II and III) are incorporated in the water pools or near the micellar core, while the pyridone moieties of **1h**, **1i**, and **1j**, having much higher hydrophobic character, are oriented into the bulk phase. Furthermore, **1h**, having a 10-carbon polymethylene chain, can bend freely but **1i** and **1j** cannot because of steric factors such that the pyridone moiety lies near the micellar surface.

Thus, our experimental results in the reversed micellar system can be interpreted as implying that 1) since in the cases of **1f** and **1g**, relatively high proportions of *cis*/*trans* and/or *cis–syn* dimers, especially at low concentration, were observed, the reactions occur in or near the water pools with folding of the detergent and a certain amount of preferential ordering of probes; 2) from the observations of a high proportion of *trans* dimer and no *syn* dimer in the case of **1h**, the reaction occurs in the bulk phase, where the molecule can be freely bent such that the two pyridone moieties are able to approach each other with a head-to-tail orientation; 3) from the completely regioselective formation of *cis* dimers and relatively high proportion of *cis–syn* dimer in the cases of **1i** and **1j**, the molecules are tightly aligned in reversed micelles, where the pyridone moieties are in contact with water molecules.

It was concluded that in the micellar system, the pyridone moieties of substrates, due to their hydrophilic character, all lie in the grooves near the micellar surface, in the Stern region, even if the molecules have a long polymethylene chain, while in reversed micelles the incorporation site of the pyridone moieties depends on the polymethylene chain length. In both micellar systems, not only the distributions of amphiphilic probes between micellar and bulk (water or cyclohexane) phases but also the orientation and incorporation site of the pyridone moiety play important roles in the regioselective formation of the *cis* dimer.

This study indicates that photochemical dimerization of amphiphilic subsrates, such as **1i** or **1j**, is possible not only in micellar but also in reversed micellar systems, and moreover, regio-control of the reactions, due to the alignment effect of micelles or reversed micelles on the substrate, should be possible.



micelle reversed micelle

Chart 2

Experimental

Melting points were determined with a Yanagimoto MP-S3 apparatus. Infrared (IR) spectra were recorded with a Hitachi 215 grating spectrophotometer, ultraviolet (UV) spectra with a Hitachi 100-50 spectrophotometer, proton nuclear magnetic resonance (^{1}H NMR) spectra with a JEOL PMX60 instrument ($CDCl_3$ as the solvent, unless otherwise stated, and $SiMe_4$ as internal standard), and mass spectra (MS) with a Shimadzu LKB 900 spectrometer. Kieselgel 60 HF_{254} (Merck), and Kieselgel 60 (Merck) and Alumina KCG 1525 (Sumitomo) were used for analytical and preparative thin-layer chromatography (TLC), and for column chromatography, respectively.

Preparation of 2-Pyridones (1b—j)——*N*-Alkyl-2-pyridones (**1b**,[16] **1c**,[17] **1d**,[16] and **1e**[18]) were prepared according to the reported procedures, and 4-propyl- and 4-heptyl-2-pyridones were prepared according to the method of Adams[19] from 2-amino-4-propyl- and 2-amino-4-heptyl-pyridines, respectively. *N*-ω-Carboxyalkyl-2-pyridones (**1f—h**) and *N*-2′-carboxyethyl-4-alkyl-2-pyridones (**1i** and **1j**) were prepared from the corresponding ω-carboxyalkyliodide and 2-pyridone or 4-alkyl-2-pyridone by a method similar to that of Räth[16]; the physical data are given in Tables V and VI.

Irradiation of *N*-Alkyl-2-pyridones (1a—e) in SL Micellar and Homogeneous Solvent Systems——The general procedure for the photoreactions was as follows; a solution of **1** in 3% aq. sodium laurate, EtOH, benzene or water was irradiated at 25 °C for 15 h with a 400 W high-pressure mercury arc lamp in a Pyrex cell through which a fine stream of nitrogen bubbles was passed. The reaction mixture was extracted with CH_2Cl_2 (after neutralization with 5% aq. HCl, when SL surfactant was used). The CH_2Cl_2 solution was dried ($MgSO_4$) and evaporated *in vacuo*. The residue was separated by silica gel preparative TLC ($CHCl_3$: MeOH = 95 : 5, v/v) to give the isomer (**2**), and dimers (**3**, **5**) and a mixture of **4** and **6**. In the preparative TLC, **4** and **6** were not separated but the ratio was easily determined by NMR spectroscopy, in which the signal of the C_4 olefinic proton of **6** appears at 5.7—6.1 ppm. The total yields and product distributions are given in Table I. The NMR data for products are listed in Table VII; the physical data for **3a**, **3b**, **3e**, **4a**, and **6a** are reported elsewhere,[10] and those for **3c** and **3d** are given in Table VIII.

Irradiation of *N*-ω-Carboxyalkyl-2-pyridones (1f—j) in CTAB Micellar and Homogeneous Solvent Systems——The general procedure for the photoreactions was as follows; a solution of **1f—j** in 0.1 M aq. CTAB [purified by recrystallization (from Tokyo Kasei)], EtOH, benzene, or water was irradiated under the same conditions as described above, and products were isolated. The reaction mixture was concentrated *in vacuo* (or after addition of an excess of tetrahydrofuran when CTAB surfactant was used). The residue was separated by silica gel column chromatography to give the isomer (**2f—j**) when the column was developed with acetone–CH_2Cl_2 (1 : 9, v/v), then a mixture of dimers with MeOH–CH_2Cl_2 (1 : 1, v/v). The mixture was reacted with MeOH–H_2SO_4 and separated by silica gel preparative TLC (acetone : CH_2Cl_2 = 1 : 9, v/v) to give methyl esters of **3**, **4**, **5** and/or **6**. The total yields and

TABLE V. Formation of the Pyridones (1f—j)

Compd.	Yield (%)	mp (°C)	Recryst. solvent	MS *m/e* (M^+)	IR$\nu_{max}^{CHCl_3}$ cm^{-1}	UVλ_{max}^{EtOH} nm (log ε)	Formula	Analysis (%) Calcd (Found)		
								C	H	N
1f	30	182—183	MeOH	167	1690[a]	227 (3.84)	$C_8H_9NO_3$	57.48	5.43	8.38
					1625	302 (3.76)		(57.70	5.35	8.32)
					1520					
1g	20	79—80	EtOH–H_2O	209	1710	229 (3.80)	$C_{11}H_{15}NO_3$	63.14	7.23	6.69
					1658	303 (3.69)		(63.22	7.34	6.81)
					1580					
1h	50	100—103	EtOH	279	1712	229 (3.75)	$C_{16}H_{25}NO_3$	68.78	9.02	5.01
					1660	303 (3.65)		(68.88	8.74	4.88)
					1587					
1i	72	160—161	EtOH	209	1725	231 (3.62)	$C_{11}H_{15}NO_3$	63.14	7.23	6.69
					1643	298 (3.66)		(63.09	6.97	6.83)
					1565					
1j	53	141—142	Benzene–MeOH	265	1722	231 (3.80)	$C_{15}H_{23}NO_3$	67.89	8.74	5.28
					1657	298 (3.83)		(67.76	8.64	5.08)
					1560					

a) In KBr.

TABLE VI. ^{1}H NMR Spectral Data for Pyridones (**1f**—**j**)

Compd.	Pyridone moiety				Others
	C_3–H	C_4–H	C_5–H	C_6–H	
1f$^{a)}$	6.32 dd $J=10, 1.2$	7.35 ddd $J=10, 6.8, 2$	6.13 td $J=6.8, 1.2$	7.62 dd $J=6.8, 2$	4.03 (t, $J=7$); N–CH_2– 2.47 (t, $J=7$); –CH_2COO–
1g	6.53 dd $J=10, 1.5$	7.2—7.5 m	6.15 td $J=6.5, 1.5$	7.2—7.5 m	3.87 (t, $J=7$); N–CH_2– 2.32 (t, $J=7$); –CH_2COO– 1.15—2.0 (m); N–$CH_2(C\underline{H}_2)_3CH_3$
1h	6.62 dd $J=10, 1.5$	7.33 ddd $J=10, 6.5, 2$	6.21 td $J=6.5, 1.5$	7.25 dd $J=6.5, 2$	3.93 (t, $J=7$); N–CH_2– 2.33 (t, $J=7$); –CH_2COO– 1.0—2.1 (m); N–$CH_2(C\underline{H}_2)_8CH_2COO$–
1i$^{b)}$	6.3—6.4 m		6.15 dd $J=7, 2$	7.48 d $J=7$	4.18 (t, $J=7$); N–CH_2– 2.82 (t, $J=7$); –CH_2COO– 2.47 (t, $J=7$); C_4–CH_2– 1.2—2.0 (m); –$C\underline{H}_2CH_3$ 0.97 (s); –CH_3
1j	6.3—6.5 m		6.13 dd $J=7, 2$	7.42 d $J=7$	4.20 (t, $J=7$); N–CH_2– 2.90 (t, $J=7$); –CH_2COO– 2.47 (t, $J=7$); C_4–CH_2– 1.1—1.9 (m); C_4–$CH_2(C\underline{H}_2)_5CH_3$ 0.90 (s); –CH_3

a) In DMSO-d_6.
b) In CD_3OD.

TABLE VII. ^{1}H-NMR Spectral Data for Isomer (**2**) and Dimers (**3**—**6**)

Compd.	Pyridone moiety				Others$^{a)}$
	C_3–H	C_4–H	C_5–H	C_6–H	
2b—**e**	4.0—4.2 m	6.55 br s		4.2—4.4 m	2.9—3.3 (m); N–CH_2– 1.1—1.9 (m); N–$CH_2(C\underline{H}_2)_n$– 0.90 (t, $J=7$); –CH_3
2f—**h**	4.0—4.2 m	6.55 br s		4.2—4.4 m	3.0—3.3 (m); N–CH_2– 2.3—2.5 (t, $J=7$); –CH_2COO– 1.0—1.9 (m); N–$CH_2(C\underline{H}_2)_n$–
2i, j	4.0—4.1 m		6.20 br s	4.1—4.2 m	3.3—3.7 (m); N–CH_2– 2.53 (t, $J=7$); –CH_2COO– 2.17 (t, $J=7$); C_4–CH_2– 1.1—1.7 (m); N–$CH_2(C\underline{H}_2)_n$– 0.90 (t, $J=7$); –CH_3
3b—**e**	3.57 ddd $J=10, 5, 2$	6.15 ddd $J=8, 5, 2$	6.60 ddd $J=8, 5, 2$	4.08 ddd $J=10, 5, 2$	3.4—4.3, 2.2—2.7 (m); N–CH_2– 1.1—1.8 (m); N–$CH_2(C\underline{H}_2)_n$– 0.87 (t, $J=7$); –CH_3
3f—**h**$^{b)}$	3.58 ddd $J=10, 6.5, 2$	6.10 ddd $J=8, 6.5, 2$	6.60 ddd $J=8, 6.5, 2$	4.0—4.3 ddd $J=10, 6.5, 2$	2.0—4.3 (m); N–CH_2–, –$C\underline{H}_2COO$– 3.67 (s); –$COOCH_3$ 0.8—2.0 (m); N–$CH_2(C\underline{H}_2)_n$–

TABLE VII (continued)

Compd.	Pyridone moiety				Others[a]
	C_3–H	C_4–H	C_5–H	C_6–H	
3i, j[b]	3.38 dd $J=10, 2$		6.1—6.3 m	4.27 dd $J=10, 7$	2.3—4.3 (m); $\mathrm{N{-}C\underline{H}_2C\underline{H}_2COO{-}}$ 3.65 (s); $\mathrm{{-}COOCH_3}$ 2.05 (t, $J=7$); $\mathrm{C_4{-}CH_2{-}}$ 1.1—1.8 (m); $\mathrm{C_4{-}CH_2(C\underline{H}_2)_n{-}}$ 0.90 (t, $J=7$); $\mathrm{{-}CH_3}$
4b—e	3.3—3.5 m	6.2—6.5 m		4.0—4.2 m	3.1—4.3, 2.2—2.5 (m); $\mathrm{N{-}CH_2{-}}$ 1.1—1.9 (m); $\mathrm{N{-}CH_2(C\underline{H}_2)_n{-}}$ 0.90 (t, $J=7$); $\mathrm{{-}CH_3}$
4f—h[b]	3.3—3.5[c] m	6.3—6.5 m		4.3—4.5 m	2.1—4.3 (m); $\mathrm{N{-}CH_2{-}}$ 3.67 (s); $\mathrm{{-}COOCH_3}$ 2.57 (t, $J=7$); $\mathrm{N{-}CH_2C\underline{H}_2COO{-}}$ 2.25 (t, $J=7$); $\mathrm{{-}(CH_2)_nC\underline{H}_2COO{-}}$ 1.0—2.0 (m); $\mathrm{N{-}CH_2(C\underline{H}_2)_nCH_2COO{-}}$
4i, j[b]	3.1—3.3 m		5.7—6.0 m	4.2—4.3 m	2.3—4.3 (m); $\mathrm{N{-}CH_2{-}}$ 3.66 (s); $\mathrm{{-}COOCH_3}$ 2.53 (t, $J=6.5$); $\mathrm{{-}CH_2COO{-}}$ 2.10 (t, $J=7$); $\mathrm{C_4{-}CH_2{-}}$ 1.1—1.8 (m); $\mathrm{C_4{-}CH_2(C\underline{H}_2)_n{-}}$ 0.90 (t, $J=6.5$); $\mathrm{{-}CH_3}$
5b—e	3.3—3.8 m	6.1—6.3 m		4.0—4.5 m	2.5—3.2, 3.3—4.8 (m); $\mathrm{N{-}CH_2{-}}$ 1.1—1.7 (m); $\mathrm{N{-}CH_2(C\underline{H}_2)_n{-}}$ 0.90 (t, $J=7$); $\mathrm{{-}CH_3}$
5f—h[b]	3.2—4.6[d] m	6.1—6.3 m		3.2—4.5[d] m	2.1—4.5 (m); $\mathrm{N{-}CH_2{-}}$ 3.63 (s); $\mathrm{{-}COOCH_3}$ 2.50 (t, $J=7$); $\mathrm{N{-}CH_2C\underline{H}_2COO{-}}$ 2.30 (t, $J=7$); $\mathrm{N{-}CH_2(CH_2)_nC\underline{H}_2COO{-}}$ 1.0—1.9 (m); $\mathrm{N{-}CH_2(C\underline{H}_2)_nCH_2COO{-}}$
5i, j[b]	3.37 dd $J=10, 2$		5.6—6.0 m	4.37 dd $J=10, 7$	2.3—4.3 (m); $\mathrm{N{-}CH_2{-}}$ 3.65 (s); $\mathrm{{-}COOCH_3}$ 2.53 (t, $J=7$); $\mathrm{{-}CH_2COO{-}}$ 1.97 (t, $J=7$); $\mathrm{C_4{-}CH_2{-}}$ 1.1—1.8 (m); $\mathrm{C_4{-}CH_2(C\underline{H}_2)_nCH_3}$ 0.90 (t, $J=7$); $\mathrm{{-}CH_3}$
6b—e	3.5—3.7 m	5.7—6.1 m	6.3—6.7 m	4.0—4.3 m	3.3—4.4, 2.1—2.8 (m); $\mathrm{N{-}CH_2{-}}$ 1.1—1.8 (m); $\mathrm{N{-}CH_2(C\underline{H}_2)_n{-}}$ 0.88 (t, $J=7$); $\mathrm{{-}CH_3}$
6f—h[b]	3.5—3.7 m	5.7—6.0 m	6.3—6.6 m	4.0—4.6 m	2.1—4.3 (m); $\mathrm{N{-}CH_2{-}}$ 3.63 (s); $\mathrm{{-}COOCH_3}$ 2.2—2.5 (t, $J=7$); $\mathrm{{-}CH_2COO{-}}$ 1.0—1.8 (m); $\mathrm{N{-}CH_2(C\underline{H}_2)_nCH_2COO{-}}$
6i, j[b]	3.2—3.4 m		6.0—6.2 m	4.3—4.4 m	2.3—4.3 (m); $\mathrm{N{-}CH_2{-}}$ 3.63 (s); $\mathrm{{-}COOCH_3}$ 2.53 (t, $J=7$); $\mathrm{{-}CH_2COO{-}}$ 1.97 (t, $J=7$); $\mathrm{C_4{-}CH_2{-}}$ 1.1—1.9 (m); $\mathrm{C_4{-}CH_2(C\underline{H}_2)_n{-}}$ 0.90 (t, $J=7$); $\mathrm{{-}CH_3}$

[a] *N*-Methylene protons of the dimers show different chemical shifts and the signals overlapped with those of other protons.

[b] As methyl esters.

[c] Shows chemical shifts of **4f**; those of **4g** and **4h** were not determined due to overlapping with other proton signals.

[d] Overlapped with signals of other protons.

TABLE VIII. Formation of the Dimers (**3c**—**j**)

Compd.	mp (°C)[a]	IR$\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}[b]	Formula	Analysis (%) Calcd (Found) C	H	N
3c	163—164	1655, 1640	$C_{22}H_{34}N_2O_2$	73.70 (73.64	9.56 9.11	7.81 7.72)
3d	138—139	1655, 1640	$C_{26}H_{42}N_2O_2$	75.31 (75.36	10.21 9.94	6.76 7.02)
3f[c]	185—186	1730, 1645	$C_{18}H_{22}N_2O_6$	59.66 (59.83	6.12 6.19	7.73 7.89)
3g[c]	160—161	1730, 1645	$C_{24}H_{34}N_2O_6$	64.55 (64.51	7.68 7.48	6.27 6.26)
3h[c]	95	1730, 1650	$C_{34}H_{54}N_2O_6$	69.59 (69.57	9.28 9.12	4.77 4.72)
3i[c]	197—198	1725, 1643	$C_{24}H_{34}N_2O_6$	64.55 (64.25	7.68 7.42	6.27 6.25)
3j[c]	145—146	1730, 1650	$C_{32}H_{50}N_2O_6$	68.78 (68.90	9.02 9.11	5.01 5.39)

a) Recrystallized from EtOH.
b) UV spectra of **3** show only end absorption.
c) As methyl esters of **3f**—**j**.

product distributions are given in Tables II and III. The NMR and other physical data for products are listed in Tables VII and VIII, respectively.

Irradiation of *N*-ω-Carboxyalkyl-2-pyridones (1f—j) in a Reversed Micellar System——A reversed micellar system composed of 0.12 M dodecylammonium acetate, 0.12 M dodecylamine, and 0.69 M water in cyclohexane was used. The general procedure for the photoreactions was as follows; a solution of **1f**—**j** in the reversed micelles was irradiated under the same conditions as described above, followed by separation of the products. An excess of water and MeOH was added to the reaction mixture. The solution was passed through an ion-exchange column (IR-120) to remove the dodecylamine, then one-half of the solution was concentrated *in vacuo* and chromatographed on a silica gel column to give the isomer (**2**). The other half of the solution was concentrated *in vacuo*, and the residue was reacted with MeOH–H_2SO_4. The mixture was separated by silica gel preparative TLC (acetone–CH_2Cl_2) to give the methyl esters of dimers. The product distributions were determined according to the method described above and are shown in Table IV.

References and Notes

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