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Organized Photodimerization of Cinnamic Acid in Cationic Reversed Micelle

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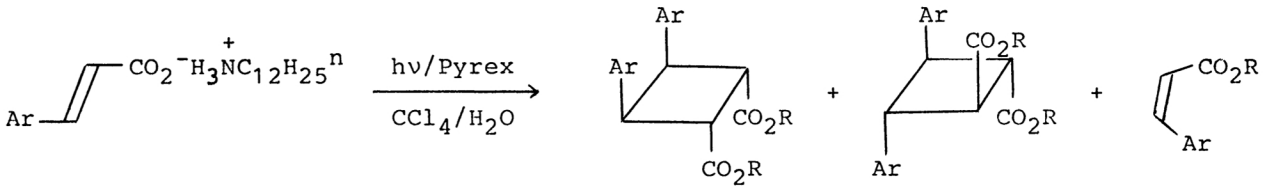
Laurylamine cinnamate salt (**1**), a reversed micelle-forming surfactant, undergoes a regioselective photodimerization to give syn- and anti-head-to-head dimers, the former being predominant. The rate of dimer formation shows a discontinuous point at the cmc of **1** (*i.e.*, 3-5 mM), which is in parallel with the change in the relative emissive intensities of the monomer and the excimer.

[2+2] Photodimerizations of olefins are useful for various synthetic applications, but are not stereoselective and inefficient in homogeneous solutions, accompanying facile cis-trans isomerizations. For example, irradiation of cinnamic acid or its methyl ester in solutions resulted in stereoisomerization predominantly.[1,2)]

Solid state photochemistry has also been successfully applied to prepare cyclobutane compounds;[3)] many examples have established that the stereochemistry of photodimers reflects a monomer packing in crystals.[4)] It is not easy, however, to predict and control the stereochemistry of photodimerization in solid crystals. On the other hand, microheterogeneous fields formed by micelles, vesicles, microemulsions or films, may provide an environment suitable for the controlled alignment of substrate olefins.[5)] In fact, a number of studies have been reported on stereoselective photochemical dimerization of olefins in such fields.[6)]

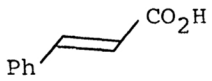
In the course of the study on photochemical dimerization in organized environments, laurylamine cinnamate salt (**1a**), a reversed micelle-forming surfactant in carbon tetrachloride or cyclohexane, is found to undergo a regioselective photodi-



1 **2** (HH) **3** (HH) **4**

a, Ar = C_6H_5; **b**, Ar = p-$MeOC_6H_4$; **c**, Ar = p-MeC_6H_4 ;
d, Ar = m-BrC_6H_4 ; **e**, Ar = α-$C_{10}H_7$

merization. Irradiation of laurylamine cinnamate salt (**1a**) in carbon tetrachloride (7.6 mM) gave syn-(**2a**, 40%) and anti-head-to-head dimers (**3a**, 9%) as well as cis-cinnamate (**4a**, 51%). The products were isolated as their methyl esters after the treatment with acidic methanol and chromatographic separation on SiO_2, and identified by ^1H NMR spectral analyses in comparison with authentic samples.[7] These results were in sharp contrast to those of the homogeneous reaction of cinnamic acid (**5**). That is, the irradiation of **5** in the absence of laurylamine gave mainly **3a** (R



5

=H) rather than **2a** (R=H) (Entry No. 1 in Table 1). The dimer formation from **5** was 17 times as slow as the case of **1a** in the reversed micelle. In fact, the photodimerization of **5** in homogeneous solutions is known to be quite inefficient.[1,2]

A photostationary equilibrium between trans- and cis-cinnamic acids was established at the early stage preceding to the cyclodimerization. The stereochemistry

Table 1. Products Distribution in the Photolysis of Olefins **1** in Reversed Micelle[a)]

Entry No.	Olefin	Concn. of olefin /mM[b)]	Solvent	Concn. of H_2O[c)] /mM	Yield of recovered olefin[d)] /%	Dimer yield /%[e)]		
						2	**3**	**2/3**
1	**5**[f)]	10.0	C_6H_{12}	0	86.1(72/28)	12.8	23.7	0.54
2	**1a**	0.61	CCl_4	0	95.2(41/59)	6.3	1.6	3.9
3	**1a**	1.51	CCl_4	0	79.4(25/75)	20.9	4.7	4.4
4	**1a**	7.56	CCl_4	0	60.0(30/70)	40.0	8.6	4.7
5	**1b**	30.0	CCl_4	0	79.8(71/29)	36.4	10.2	3.6
6	**1c**	30.0	CCl_4	0	83.7(32/68)	17.3	4.9	3.6
7	**1d**	30.0	CCl_4	0	56.5(81/19)	56.8	23.4	2.4
8	**1e**	30.0	CCl_4	0	55.8(83/17)	63.9	18.7	3.4
9	**1a**	10.0	C_6H_{12}	0	74.6(29/71)	24.7	7.6	3.3
10	**1a**	10.0	C_6H_{12}	1.1	68.4(23/77)	24.6	13.0	1.9
11	**1a**	10.0	C_6H_{12}	3.3	75.2(22/78)	18.2	11.4	1.6
12	**1a**	10.0	C_6H_{12}	5.6	64.9(17/83)	20.1	19.4	1.0

a) Irradiation in a Pyrex vessel for 10 h. b) 1 mM = 1 mmol dm^{-3}. c) Added water. d) Combined percentages of trans (**1**) and cis olefins (**4**). Values in parentheses were the ratios of **1**/**4**. e) Determined by HPLC and NMR analyses. Figures show the product distributions among **2**, **3**, and **4**. f) Control experiment: irradiated in a homogeneous solution without laurylamine.

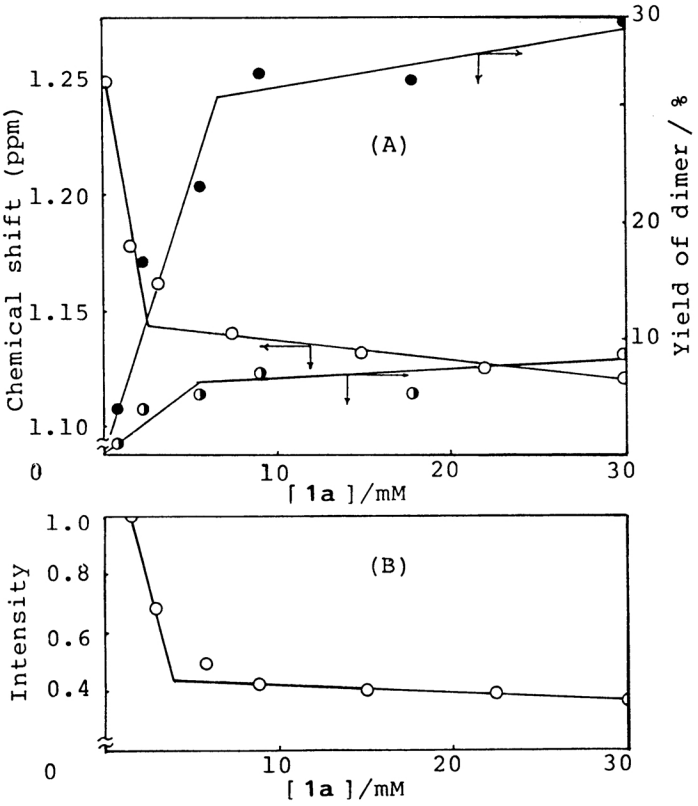


Fig. 1. Dependence of chemical shift of methylene protons of **1a** and the dimer yields (%) (A) and the fluorescence intensity of **1a** (B) upon the concentration of **1a** in CCl_4.

of **2a** and **3a** shows that trans olefin is solely responsible for the dimerization.

In a similar manner, other substituted cinnamates of laurylamine (**1b-e**), upon >300 nm light irradiation, gave the corresponding syn- and anti-dimers (**2** and **3**, respectively) and their regioselectivities were dependent on the substituents. There was little difference in the regioselectivity between phenyl(**1a**) and a bulkier α-naphthyl groups (**1e**).

A discontinuous point was observed at *ca.* 5 mM **1a** for the plots of quantum yields for dimer formation *vs.* [**1a**] as shown in Fig. 1A and Entry No. 2-4 in Table 1, while the ratio of **2a** / **3a** remained almost constant *ca.* 4:1. These observations tell us that the salt molecules are settled in a topologically organized circumstance formed by the reversed micelle aggregation. In fact, salt **1** was solubilized in cyclohexane or carbon tetrachloride as a clear solution, reflecting that **1** itself forms a reversed micelle in nonpolar solvents. A critical micelle concentration(cmc) and the aggregation number(N_A) were estimated from the NMR chemical shifts of methylene protons as a function of [**1a**] as developed by Fendler (Fig. 1A).[8] The resulting cmc and N_A in carbon tetrachloride were 2-5 mM and 2-3, respectively, which are comparable with those of laurylamine propionate, a typical surfactant for a reversed micelle.[9]

As shown in Fig. 2, the fluorescence maximum of **1a** shifts from 325 to 370 nm on going from 3.0 to 22.4 mM concentration in cyclohexane, the former and the latter being assigned to the monomer and the excimer emission, respectively. The

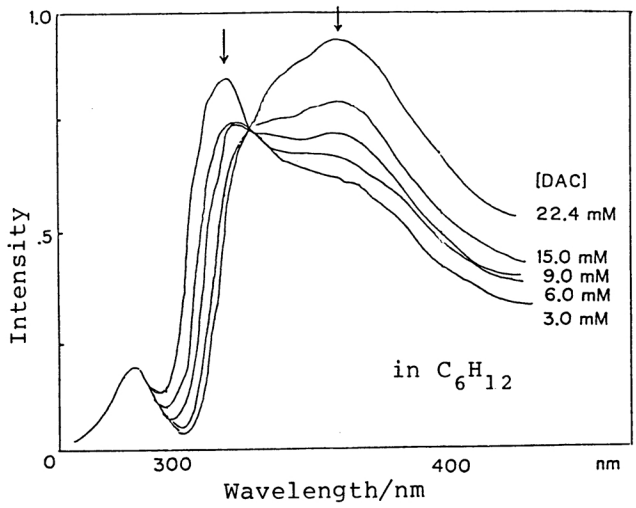


Fig. 2. Concentration dependence of emission spectra of **1a** in cyclohexane. Excitation at 280±10 nm.

plot of the fluorescence intensity against [**1a**] shows again a discontinuous point at *ca.* 5 mM, *i.e.*, the cmc of **1a** as shown in Fig. 1B.[10] All of these facts clearly demonstrate that cinnamate anions incorporated in the reversed micelle are aligned quite favorably for formation of syn-head-to-head dimer (**2**).

Finally, it is interesting to note that the addition of water considerably affects the regioselectivity of the cyclic dimers (see Entry No.9-12 in Table 1). On addition of 5.5 equivalents of water, the ratio of **2a** to **3a** decreases from 4.4 to 1.0. It is known that the addition of excess water forms a water pool in the reversed micelle core and increases the N_A values significantly.[11] In the present case, the intensity of the excimer fluorescence at 370 nm was lowered gradually by adding water. This probably means that a larger aggregation of **1** and water would break the packing of olefins organized suitably for the formation of exciplex leading to the selective head-to-head cyclodimerization.

In summary, a reversed micelle formed by laurylaminium salts serves an organized reaction field for regioselective dimerization of anionic olefins.

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