Regioselective Photodimerization of Cinnamic Acid in a Micellar Solution

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Irradiation of *trans*-cinnamic acid (**1**) and its methyl ester (**2**) in 1% aq. cetyltrimethylammonium bromide gave dimeric products in 35 and 29% yields as a mixture of truxinic and truxillic acids in a ratio of 19 : 1 and 3.8 : 1, respectively, while in homogeneous solutions (**1**) gave no photodimers and (**2**) gave dimeric products in 2.3% yield under similar reaction conditions.

The photodimerization of cinnamate groups has been studied for a long time, especially in a matrix.[1] For example, photocycloaddition in liquid ethyl cinnamate and in cinnamate glasses as a probe into the micromorphology of the solid has recently been reported by Reiser.[2] It is also well known that the photoreaction of crystalline cinnamic acid gives a crystal lattice-controlled dimer,[1] but in solution gives no photodimers.[3] We have recently investigated the photodimerization of acenaphthylene and pyridone derivatives using micellar systems.[4] We now report the successful regioselective photodimerization of (**1**) in micellar solution.

The cationic surfactant, cetyltrimethylammonium bromide (CTAB) was chosen as surfactant for (**1**) and methanol, methanol–water, and water† were used as homogeneous solvents for comparison with the micellar system. The results are given in Tables 1 and 2. For example, irradiation of (**1**) (22 mM) in 1% aq. CTAB gave dimeric products‡ (36% yield as methyl esters) as a mixture of regio- and/or stereo-isomers§ of (**3**), (**4**), (**6**), (**7**), and (**9**) in a ratio of 38:8:47:2:5, respectively, and *cis*- and *trans*-cinnamic acids (28% yields as methyl esters).

As shown in Table 1, the photodimerization of (**1**), or its sodium salt, in 50% aq. methanol or water under similar conditions gave no dimeric products. The reaction of (**2**) in methanol gave a mixture of truxinic and truxillic acids in low yield (3 : 1). In contrast, the reactions in the micellar system

$PhCH{=}CHCO_2R$ (*trans*)
(**1**) R = H
(**2**) R = Me

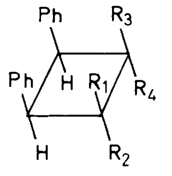
Table 1. Photodimerization of (**1**) and (**2**) in homogeneous and micellar solutions.[a]

Substrate	Solvent	% Conversion[b]	% Yield[c] of dimers	Ratio of truxinic : truxillic acids
(**1**)	1% aq. CTAB	75	36	19:1
(**2**)	1% aq. CTAB	72	29	3.8:1
(**1**)	50% aq. MeOH	40	0[d]	—
(**1**)[e]	H_2O	41	0[d]	—
(**2**)	MeOH	30	2.3	3:1

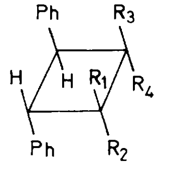
[a] In all the photoreactions, the solutions (22 mM) of (**1**) and (**2**) in homogeneous solvents or the surfactant were irradiated using a 100 W high-pressure mercury arc lamp in a Pyrex cell with a fine stream of argon bubbles at 20 °C for 20 h. [b] Based on isolated cinnamic acids. [c] Isolated yields. [d] Not observed on TLC. [e] Sodium salt of (**1**) was used in water.

Table 2. Distribution of dimeric products in the reaction of (**1**) and (**2**) using a micellar system.

	Product ratio										
	Truxinic acids						Truxillic acids				
Substrate	(**3**)	(**4**)	(**5**)	(**6**)	(**7**)	(**8**)	(**9**)	(**10**)	(**11**)	(**12**)	(**13**)
(**1**)	38	8	0	47	2	0	5	0	0	0	0
(**2**)	26	13	0	32	8	0	6	2	0	13	0

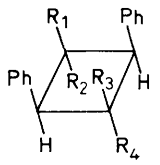


(**3**) $R_1 = R_3 = H$,
$R_2 = R_4 = CO_2H$
(**4**) $R_1 = R_4 = H$,
$R_2 = R_3 = CO_2H$
(**5**) $R_1 = R_3 = CO_2H$,
$R_2 = R_4 = H$

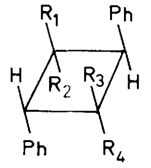


(**6**) $R_1 = R_4 = CO_2H$,
$R_2 = R_3 = H$
(**7**) $R_1 = R_3 = H$,
$R_2 = R_4 = CO_2H$
(**8**) $R_1 = R_4 = H$,
$R_2 = R_3 = CO_2H$

Truxinic acids



(**9**) $R_1 = R_3 = H$,
$R_2 = R_4 = CO_2H$
(**10**) $R_1 = R_4 = CO_2H$,
$R_2 = R_3 = H$
(**11**) $R_1 = R_3 = CO_2H$,
$R_2 = R_4 = H$



(**12**) $R_1 = R_4 = CO_2H$,
$R_2 = R_3 = H$
(**13**) $R_1 = R_3 = CO_2H$,
$R_2 = R_4 = H$

Truxillic acids

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† Sodium cinnamate was used in water.

‡ The dimeric products (**3**), (**4**), (**6**), and (**12**) from the reaction of (**1**) and (**2**) were each isolated as pure compounds, and (**7**), (**9**), and (**10**) were obtained as a mixture by anion exchange column chromatography to remove the surfactant, followed by methylation with diazomethane in the case of (**1**), then silica gel column chromatography, eluting with hexane–acetone (95:5—9:1).

§ The structures of these cyclobutane derivatives were established by comparison of the 60 MHz ^1H n.m.r. data with the literature,[2,5] and by consideration of the chemical shifts and coupling constants of the cyclobutane and/or aromatic ring protons for the 270 MHz ^1H and two dimensional n.m.r. spectra. The product ratios of the mixtures from which single product could not be isolated were established on the basis of the integral ratios of the protons in the 270 MHz ^1H n.m.r. spectrum.

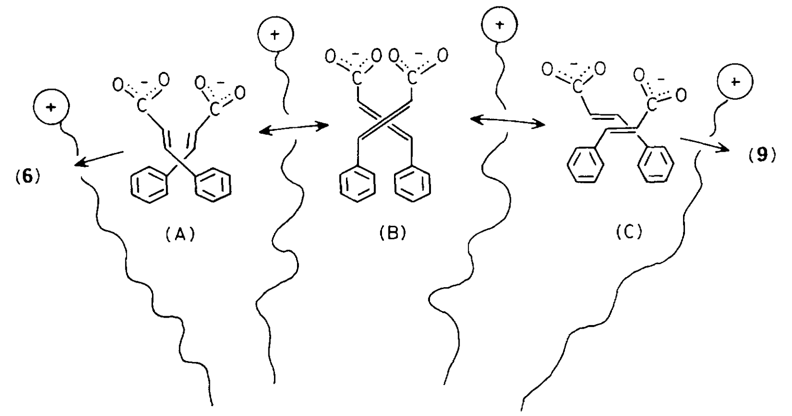

Figure 1. Possible orientations of micelles and substrates for formation of truxinic, *e.g.* (**6**), or truxillic acids, *e.g.* (**9**).¶

gave the following results. (i) The dimeric products of the reactions of (**1**) and (**2**) were obtained in 36 and 29% yields, respectively; dimerization may occur owing to the condensation effect of micelles on the substrate. (ii) The reaction of (**1**) is far more regiospecific than that of (**2**), the ratios of truxinic to truxillic acids were 19 : 1 and 3.8 : 1, respectively; truxillic acid (**9**)¶ should be obtained from (**1**) if the micelles adopt orientation (C) shown in Figure 1, since the other truxillic acids (**10**) and (**12**) obtained from (**2**) were not observed. The reactions in the micellar system indicate that all the dimeric products obtained in the reaction of (**1**) are produced by a regioselective reaction controlled by the alignment of the micelles on the substrate.

Received, 19th November 1987; Com. 1691

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¶ As shown in Figure 1, truxillic acid (**9**) should be obtained from arrangement (C) but not (B); methyl *m*-bromocinnamate, which has a (B)-type packing arrangement in the crystalline form, so that the distance between centres of adjacent double bonds is only 3.93 Å but the double bonds are not parallel, does not give photodimers.[1]