

Organized Photocyclodimerization of Laurylammonium Indene-2-carboxylate Aggregate

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Irradiation of laurylammonium indene-2-carboxylate **1**, a self-associating photoreactive surfactant, gives rise to stereoselective formation of *syn*- **2** and *anti* head-to-head dimers **3** depending upon the choice of solvent.

Recent attention focussed on the unique role of microheterogeneous fields in controlling photoreactions,¹ has shown that molecular aggregates of micelles serve as intriguing reaction media for efficient photocycloaddition of organized olefins.²⁻⁴ Thus, the photolysis of laurylammonium cinnamate gave the head-to-head dimers, β - and δ -truxinic acids in CCl_4 .⁴ Since the aggregation structure depends on the alkylammonium carboxylate concentration and the solvent employed,⁵ it may influence the regio- and/or stereo-chemistry of particular photochemical reactions. Here we report on a novel stereoselective photodimerization of laurylammonium indene-2-carboxylate **1** which may be controlled in the presence of dispersing solvents.

Irradiation of **1**† (5 mmol dm^{-3}) in CCl_4 by Pyrex-filtered light (>290 nm) under Ar gave the *syn* head-to-head **2** (β -isomer) in addition to small amounts of *anti* head-to-head **3** (δ -isomer) and *anti* head-to-tail dimers **4** (ϵ -isomer); the quantum yields were 0.11, 0.02 and 0.02, respectively. The other isomer, *syn* head-to-tail dimer **5** (α -isomer) was not observed in the reaction mixture.‡ Here, the presence of laurylamine is necessary for the photodimerization. For example, an homogeneous solution of methyl indene-2-carboxylate **6** in CCl_4 was quite resistant to photodimerization under similar conditions; *i.e.*, the quantum yield for its consumption was only 0.006 (product ratio: **2**:**3**:**4** = 24:16:60). The overall quantum yield for formation of the cyclodimers **2-5** increased with increasing concentration of **1**, a discontinuity occurring at *ca.* 2.0 mmol dm^{-3} (see Fig. 1). The critical micelle concentration of the reversed micelle **1** in CCl_4 was estimated according to Fendler's procedure⁶ to be 0.65 mmol dm^{-3} with an aggregation

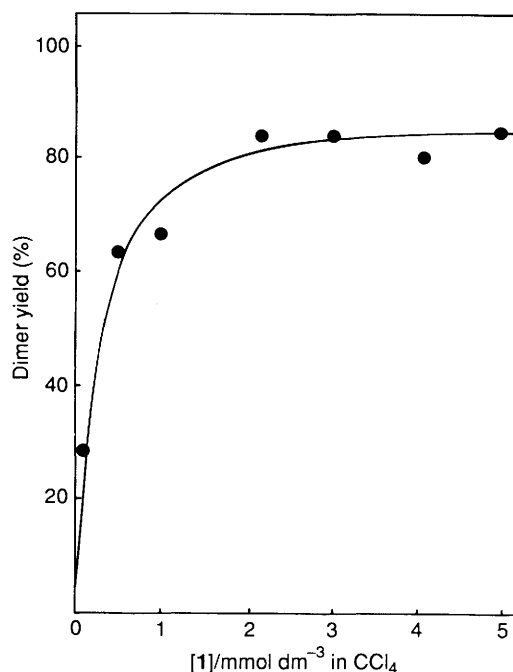


Fig. 1 Effect of the concentration of **1** on the total yields of cyclodimers; irradiation time: 30 min

number (N_A) of 2.8,§ which is comparable with the above described discontinuity in Fig. 1. Thus, small aggregates consisting of 2-3 molecules of **1** cause the effective

† Prepared by dissolving an equimolar mixture of laurylamine and indene-2-carboxylic acid in methanol, stirring for 1 h, and then rotary evaporation *in vacuo*.

‡ Products were determined by means of GLC after the conversion into methyl esters by CH_2N_2 .

§ Since the figure is too small for the term of micelle to be used, these small aggregates may, rather, be termed premicelles. Laurylammonium propionate, a typical reversed micelle-forming surfactant, has N_A 3-7 in benzene (ref. 5).

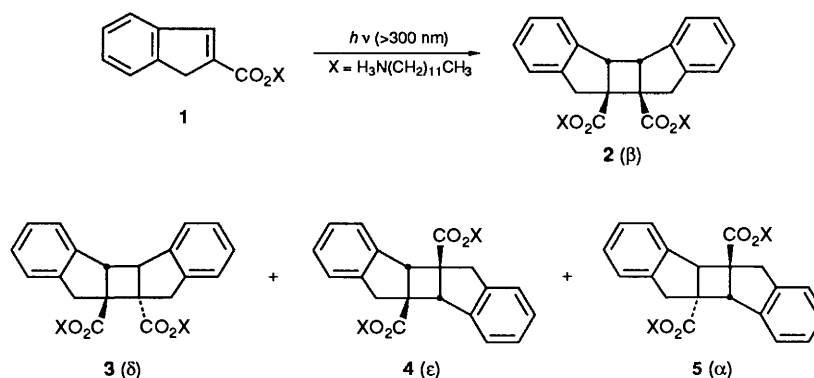


Table 1 Solvent effect on isomer distributions from irradiation of **1** and **6**^a

X in 1	Solvent	Isomeric cyclodimer (%)			
		2 (β)	3 (δ)	4 (ϵ)	5 (α)
$\text{H}_3\text{N}(\text{CH}_2)_{11}\text{Me}$ 1 ^b	CCl_4	72	13	14	—
	C_6H_6	74	12	14	—
	C_6H_6 ^c	74	10	16	—
	CHCl_3	54	19	28	—
	MeOH	—	85	11	4
	MeCN	—	88	12	—
Me 6 ^d	CCl_4 ^e	24	16	60	—
	C_6H_6	8	29	37	26
	CHCl_3	—	29	29	42
	MeOH	27	27	22	24
	MeCN	21	26	26	27

^a Conversion: 30–55%. ^b Irrad. time of 0.5 h. ^c Dried by distillation over calcium hydride. ^d Irrad. time of 3 h. ^e Chlorinated methyl indene-2-carboxylates were also detected by GC-MS analyses.

photocyclodimerization. The significance of the self-aggregation of **1** is also supported by the inefficient and non-selective photodimerization of **6**.

A pronounced solvent effect on the cyclodimer selectivity was

noted in the photolysis of **1** (Table 1). That is, the β -cyclodimer **2** was preferentially formed on irradiation of **1** in non-polar solvents, e.g., benzene, while the δ -isomer **3** was selectively obtained in polar solvents such as acetonitrile. This behaviour is in contrast to that of **6**, which gave non-selective formation of mixtures of **2**–**5** in both benzene and acetonitrile.

A detailed study is now in progress in order to clarify the origin of the above described selectivity.

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