Reactions Using Micellar System: Photochemical Dimerization of Acenaphthylene

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Summary The photochemical dimerization of acenaphthylene in micelles of nonionic and anionic surfactants gives good yields (>90%) of photodimers even with low concentrations which gave no dimeric products in benzene solution.

INTERESTING reactions using micellar systems such as micellar-catalysed hydrolysis[1] and phase transfer-catalysed reaction[2] have been studied recently, but photochemical reactions in micellar systems have not given satisfactory results.[3] We now report the successful photodimerization of acenaphthylene using micellar systems.

We have used acenaphthylene (I) as a representative of a hydrophobic substrate for studying the reaction in micellar systems, since its photodimerization in organic solvents has been studied extensively.[4] We selected polyoxyethylene-polyoxypropylene cetyl ether (Nikkol PBC-34) and sodium dodecyl sulphate (SDS) as typical nonionic and anionic surfactants, respectively, and have used benzene as a typical organic solvent to compare with the micellar systems. The results are given in the Table. For example, irradiation of acenaphthylene (I) (37 mg; 4·9 mM) (M ≡ mol l^{-1}) in 1% aq. PBC-34 gave a dimeric product (36 mg, 97% yield), as a mixture of *cis*- and *trans*-stereoisomers (II) and (III)[†] in a ratio of 0·77 : 1, estimated from integration of the methine n.m.r. signals.[‡]

TABLE. Dimerization of acenaphthylene (I).[a]

Solvent	Conc./mM	% Recovered (I)	% Yield of (II) + (III)	Ratio (II) : (III)
Benzene	1340	86·9	9·8	22·3 : 1
	100	84·0	8·2	14·4 : 1
	24	91·1	8·1	3·5 : 1
	3·2	97·9	0	
1% aq. PBC-34	4·9[b]	0	97·3	0·77 : 1
	4·9[b,c]	0	98·4	1·06 : 1
	1·9	0	85·4	0
5% aq. PBC-34	19[b]	0	94·5	0·80 : 1
	9·7	0	93·3	0·78 : 1
	1·9	0	91·2	0·13 : 1
10% aq. PBC-34	28[b]	0	96·0	0·88 : 1
	19	0	95·1	0·93 : 1
	1·9	0	94·4	0·06 : 1
5% aq. SDS	9·7	0	96·5	2·7 : 1

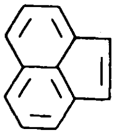
[a] In all the photoreactions, solutions of (I) in benzene or the surfactant were irradiated by a 100 W high-pressure mercury arc lamp in a Pyrex cell with a fine stream of N_2 bubbles at 17—25 °C for 4 h. [b] Saturated solution. [c] Bubbled continuously with a fine stream of air. The change in the ratio of (II) to (III) was consistent with the reported effect of oxygen (ref. 4), which promotes formation of the *cis*-dimer.

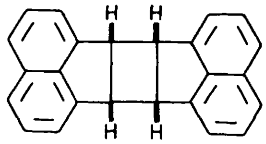
[†] After purification by t.l.c. (silica gel, benzene–n-hexane, 3 : 1), the dimeric product gave the *cis*-dimer (II) (m.p. 233—235 °C; 16·2 mg) and the *trans*-dimer (III) (m.p. 307—309 °C; 19·3 mg) in the ratio 0·84 : 1 (ref. 4).

[‡] Recorded in $CDCl_3$ with Me_4Si as internal standard with a JNM-PMX60 spectrometer. The methine protons of (II) and (III) appear as singlets at δ 4·90 and 4·10, respectively. The latter is shielded by the anisotropic effect of aromatic ring.

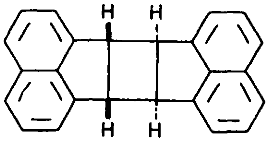
As shown in the Table, the photodimerization of (I) in benzene under similar irradiation conditions gave generally low yields (<10%), the ratio of *cis* (II) to *trans* (III) dimer increasing with increasing concentration of (I). At a concentration of 3·2 mM, no dimeric products were observed in benzene. In contrast, the reactions in the micellar systems gave the following results: (i) yields of dimeric products were high (85·4—98·4%); (ii) in the concentration range 5—30 mM, the ratios of (II) to (III) were almost independent of the initial concentration of (I), whereas for very low concentrations of (I) (1·9 mM), formation of the *trans*-dimer (III) was preferred, *i.e.*, the course of the reaction depends upon the concentration of substrate at low concentrations; (iii) the concentration of the surfactant in the micellar systems has little influence on the ratio of (II) to (III); (iv) the ratio of (II) to (III) depends on the surfactant used (Table; 9·7 mM conc.).

In conclusion, photochemical dimerization of hydrophobic substrates, such as (I), is possible in aqueous media by using the solubilization effect of micellar systems, and quantitative reactions, due to the condensation effect of micelle on the substrate, should be possible.


(I)



(II)



(III)

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