

Photochemical Polar Addition of 1,1-Diphenylethene Using Photosensitive Surfactant in Stable Oil-in-Water Emulsion

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(Received July 1, 2004; CL-040772)

An aq NaOH solution of the photosensitive surfactant **1** was mixed with 1,1-diphenylethene **2** to form a stable oil-in-water emulsion and excitation of the emulsion afforded the alcohol **3** in good yield without stirring. The photosensitive surfactant **1** works more efficiently in heterogeneous system (in water) than in homogeneous system (in organic solvent).

Recently, water as organic reaction medium has been attracted much attention from ecological and environmental viewpoints.^{1,2} A photoreaction in water may offer many advantages, since light is clean and powerful reagent to transform organic molecules. However, considerable limitation of photoreaction in water is encountered with the low solubility of organic molecules in water.³ In order to solve the problem, the surfactant **1**⁴ is designed in which the naphthyl group is attached to hydrophobic part as photosensitizer (Figure 1). This surfactant **1** could provide the hydrophobic reaction field for organic molecules through emulsion formation in water, where the photosensitive site would come into contact with the substrates effectively. Although photochemical reactions in surfactant solutions have been investigated,⁵ the photoreaction in water using this type of surfactant has never been studied. We now report that when an aq NaOH solution of the photosensitive surfactant **1** was mixed with 1,1-diphenylethene **2**, a stable oil-in-water emulsion was formed and excitation of the mixture afforded the alcohol **3** in good yield.

An aq solution (20 mL) containing NaOH (25 mM) and the

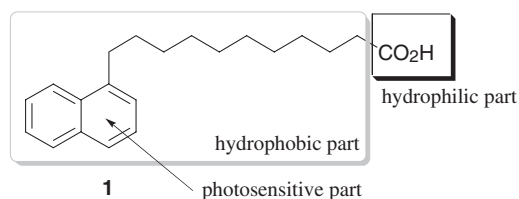


Figure 1. Photosensitive surfactant **1**.

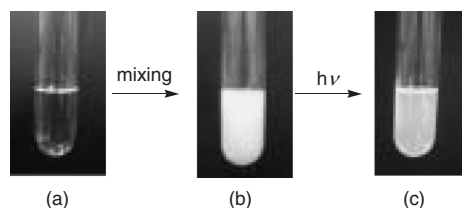
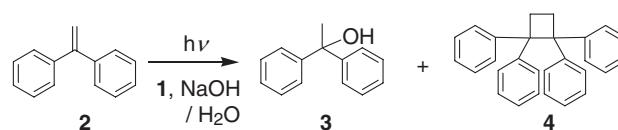


Figure 2. (a) The aq NaOH solution containing **1** and **2**, (b) after mixing for 12 h, a white dispersion (emulsion) was formed, (c) after irradiation for 12 h without stirring.

surfactant **1** (10 mM) was mixed vigorously under argon atmosphere with 1,1-diphenylethene **2** (10 mM) for 12 h to form a stable oil-in-water emulsion (a white dispersion, Figure 2b). The oily particles including the surfactant **1** and the organic substrate **2** were dispersed stably in water, and this particle size was proved to be 300 nm.⁶ This emulsion was irradiated with a 500-W high-pressure mercury lamp through a Pyrex filter (>280 nm) for 12 h at room temperature without stirring. The mixture was neutralized by 1 M HCl and extracted with ethyl acetate. Purification of the crude product by column chromatography on silica gel afforded 1,1-diphenylethanol **3** (64%), 1,1,2,2-tetraphenylcyclobutane **4** (8%), and recovery of **2** (19%) in isolated yields, respectively (Scheme 1, Entry 1 in Table 1). In addition, the surfactant **1** could be recovered in 93% yield.



Scheme 1.

The effects of solvent and surfactant on this photoreaction were investigated under various conditions. As can be seen from Table 1, the alcohol **3** was given in good yield only by using the photosensitive surfactant **1** in aq NaOH solution (Entry 1). Without NaOH, the surfactant **1** was not dissolved in water, and excitation of the mixture gave a trace of **4** (Entry 2). In homogeneous system (an aq acetonitrile solution, water:acetonitrile = 1:9), the mixture was irradiated to produce **3** in very low yield (Entry 3). When the dispersion of **2** in an aq NaOH solution was excited in the absence of **1**, **4** was only obtained (Entry 4). Addition of

Table 1. Effects of solvent and surfactant on the photoreaction

Entry	Surfactant ^a	Solvent	Additive	Yield / % ^b		Recovery / %	
				3	4	1	2
1	1	H ₂ O	NaOH ^c	64	8	93	19
2	1	H ₂ O	—	0	<1	85	60
3	1	H ₂ O-CH ₃ CN ^d	—	1	0	98	93
4	—	H ₂ O	NaOH ^c	0	8	—	71
5	—	H ₂ O	NaOH ^c , 1-MN ^e	0	<1	—	72
6	Lauric acid ^f	H ₂ O	NaOH ^c	0	24	—	71
7	Lauric acid ^f	H ₂ O	NaOH ^c , 1-MN ^e	0	2	—	85

^a10 mM. ^bIsolated yield. ^c25 mM. ^dH₂O:CH₃CN = 1:9. ^e1-MN = 1-methylnaphthalene (10 mM). ^fCH₃(CH₂)₁₀CO₂H.

1-methylnaphthalene (1-MN) as photosensitizer also resulted in no formation of the alcohol **3** (Entry 5). Instead of **1**, use of lauric acid, which is the surfactant having no photosensitive part, did not lead to formation of **3** both in the absence (Entry 6) and presence (Entry 7) of 1-MN. These results clearly indicate that the photosensitive surfactant **1** promotes the formation of the alcohol **3** through the formation of emulsion in heterogeneous system (in water). In contrast, the surfactant **1** does not work efficiently in homogeneous system (in organic solvent).

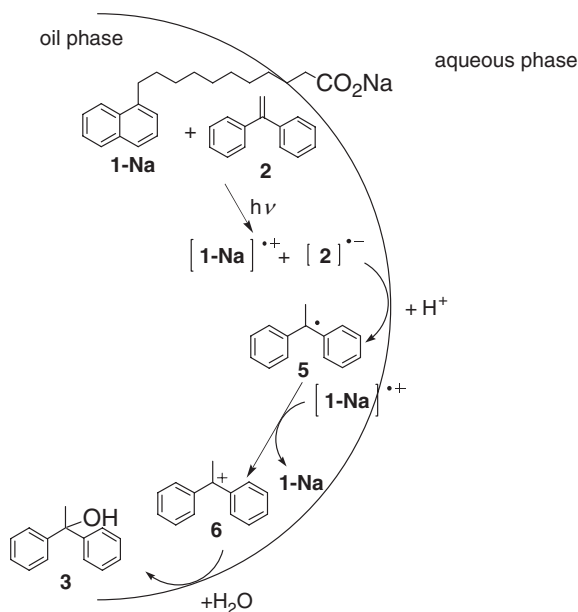


Figure 3. Proposed mechanism of this photoreaction in emulsion.

Figure 3 shows a proposed mechanism of the photoreaction in the emulsion system. Arnold et al. previously reported that an aqueous acetonitrile solution of 1-MN and **2** was irradiated to give **3** via photoinduced electron transfer (homogeneous condition).⁷ In heterogeneous system, 1-MN did not work as electron donor both in the absence (Entry 5 in Table 1) and presence (Entry 7) of lauric acid at an oil–water interface. On the other hand, the photosensitive surfactant **1** efficiently serves as electron donor (Entry 1). These results suggest that the surfactant **1** could work at the interface and be preferably used in heterogeneous photoinduced electron-transfer reaction. At first, excitation of the emulsion of **1** and **2** produces the radical anion of **2** via electron transfer, and successive protonation at the unsubstituted end generates the radical **5**. Back electron transfer to the radical cation of **1** affords the cation **6**, which is trapped by water at the interface. Low yield formation of the alcohol **3** in homogeneous solution (aq acetonitrile solution) is attributable to low local concentrations of the photosensitizer **1** and the substrate **2**. The oily particles including the surfactant **1** and the hydrophobic substrate **2** are formed in water, which provides the high local concentrations of **2** and alkylnaphthalene part. This situation in emulsion causes the predominant formation of **3**.

In conclusion, we have found that the photochemical reaction in emulsion system using the photosensitive surfactant could be used for clean process to transform organic materials.

Investigations of the scope, limitation and application of photo-reactions in this emulsion system are currently in progress.

This work was supported by a Grant-in-Aid for Scientific Research (No.15750081) from the Japan Society of Promotion of Science. We thank to Dr. Kiyoshi Suzuki, Department of Materials Science and Engineering, Faculty of Engineering, University of Fukui, for helping DLS measurement and discussion.

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