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Tetrahedron Letters 47 (2006) 3257–3260

Tetrahedron Letters

# Redox-photosensitized reaction of indene using photosensitive surfactant in emulsion: dependence on oil droplet size and surfactant charge

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Received 3 February 2006; revised 3 March 2006; accepted 8 March 2006
Available online 23 March 2006

**Abstract**—A redox-photosensitized reaction of indene **2** using a photosensitive surfactant **1a** in an oil-in-water emulsion proceeded efficiently to give alcohol **3** as a major product and is strongly influenced by the oil droplet size and surfactant charge.

In the recent past, photochemical reactions in microheterogeneous systems, such as micelles, emulsions, and vesicles, have been actively investigated.[1] For example, the photoinduced electron transfer between hydrophilic and hydrophobic solutes has been suggested to mimic photosynthetic pathways since this partition between these solutes could retard the recombination of oxidized and reduced species.[2] In particular, efficient charge separation between reactive species would be achieved in microheterogeneous media. However, there have been few previous reports on organic photochemical reactions in such systems.[3] We have recently reported that the photochemical polar addition by using a photosensitive surfactant proceeded smoothly in a microheterogeneous system.[4] With regard to this, our attention is confined to a redox-photosensitized reaction in this system. The redox-photosensitized reaction is a remarkable electron transfer process since a photosensitizer can act as a redox carrier. Thus far, studies have been carried out in homogeneous systems such as methanol–acetonitrile and water–acetonitrile solutions.[5] In this letter, we would like to report that the photosensitive surfactant **1a**[6] in which the naphthyl group is attached to hydrophobic part as photosensitizer (Fig. 1) can be utilized successfully in a redox-photosensitized reaction in a microheterogeneous system in water. Detailed experiments showed that the characteristic feature of the emulsion system is that the efficiency of this photoreaction is highly dependent on the oil droplet size and the charge of the surfactant used.

An oil-in-water emulsion was formed when an aqueous solution of the surfactant **1a** (5 mM) was mixed with the indene **2** (10 mM), 1,4-dicyanobenzene (DCB, 3 mM),

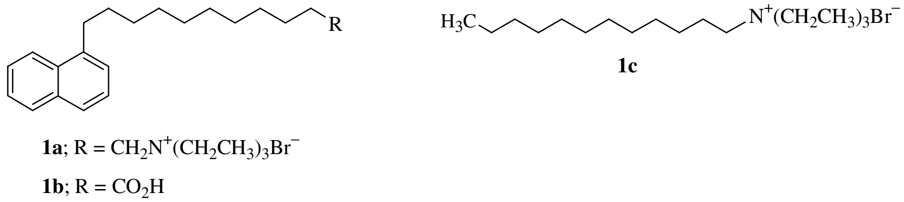

**Figure 1.** Photosensitive surfactants **1a**, **b** and non-photosensitive surfactant **1c**.

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*Keywords*: Redox-photosensitized reaction; Photosensitive surfactant; Emulsion; Oil droplet size; Surfactant charge.

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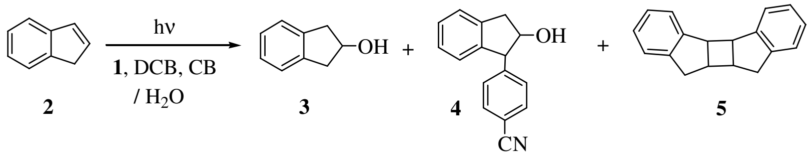
doi:10.1016/j.tetlet.2006.03.038



**Scheme 1.**

and cyanobenzene (CB, 30 mM) under an argon atmosphere for 12 h. The emulsion was irradiated with a 500 W high-pressure mercury lamp through a Pyrex filter (>300 nm) under vigorous stirring for 24 h at room temperature to afford mainly 2-indanol **3** (31%) accompanied by **4** (4%) and the dimer **5** (1%) in isolated yields (Scheme 1, entry 1 in Table 1).[7] In the absence of CB, DCB dissolved little in the mixture, and the yield of the photoproduct **3** was very low (4%). The use of benzene in the place of CB produced a low yield of **3** (4%). Thus, CB serves as a polar medium in this system and this photoreaction takes place in the oil droplet of CB in water.

The results of our study, in which we investigated the effects of additives and solvents, are shown in Table 1. When the mixture was irradiated in the absence of **1a**, alcohol **3** was not obtained (entry 2). Instead of **1a**, the addition of 1-methylnaphthalene as photosensitizer resulted in a low yield of **3** (entry 3). The use of the surfactant **1c** that had no photosensitizer activity was not effective both in the absence and presence of 1-methylnaphthalene as compared with **1a** (entries 4 and 5). In a homogeneous system (aqueous acetonitrile solution; water/acetonitrile = 1:9), a low yield of alcohol **3** was observed (entry 6). These results indicate that the formation of an emulsion provides high local concentrations of the reactant and the alkylnaphthalene part of **1a** as photosensitizer; in this emulsion, the surfactant **1a** serves efficiently as a mediator for photochemical electron transfer leading to a higher yield of **3**.

Next, we studied the effect of oil droplet size on the reaction course. In the absence of stirring, the yield of **3** decreased, implying that stirring is essential to retain the particle size (entry 7). The particle size formed in entry 1 was proven to be 600 nm by dynamic light scattering measurement.[8] Further addition of **1a** (7.5 mM) caused a decrease in the oil droplet size (370 nm) and an increase in the yield of **3** (50%, entry 8). However, when the concentration of **1a** was greater than 10 mM, a clear solution was formed due to a decrease in the oil droplet size, and the yield of **3** was lower (entries 9 and 10).[9] The best result was achieved by the addition of cetyltrimethylammonium bromide (CTAB, $CH_3(CH_2)_{15}N^+$-$(CH_3)_3Br^-$, 1 mM) in the presence of **1a** (5 mM). The addition of CTAB decreased the droplet size (500 nm) and yielded 63% of alcohol **3** (entry 11). Higher concentrations of CTAB caused a decrease in the yield similar to that observed in the case of **1a** (entries 12 and 13). It was found that a small particle size resulted in a higher yield of **3**; however, a decrease in this size below a certain limit reduced the yield of **3**.

The anionic surfactant **1b** was also examined. When the emulsion containing the anionic surfactant **1b** (5 mM), NaOH (25 mM), **2** (10 mM), DCB (3 mM), and CB (30 mM) was subjected to the photoreaction, a 23% yield of the decarboxylated product **6** was obtained along with the recovery of **1b** (38%) and a poor yield of **3** (1%), as shown in Scheme 2.[10] The yield of the decarboxylated product **6** was observed to be low (6%) in the absence of **2**, and **6** was not obtained when DCB was not added. From these results, we noted that

**Table 1.** Product yields in a redox-photosensitized reaction of **2** under various conditions

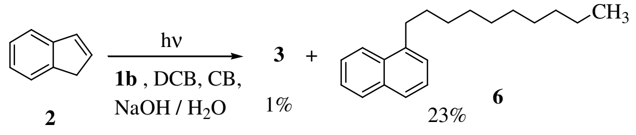
| Entry | Surfactant (mM) | Additive[a] | Product yields/%[b] | | |
|---|---|---|---|---|---|
| | | | **3** | **4** | **5** |
| 1 | **1a** (5) | DCB, CB | 31 | 4 | 1 |
| 2 | — | DCB, CB | 0 | 0 | 9 |
| 3 | — | DCB, CB, 1-methylnaphthalene | 9 | 6 | Trace |
| 4 | **1c** (5) | DCB, CB | 0 | 6 | 15 |
| 5 | **1c** (5) | DCB, CB, 1-methylnaphthalene | 13 | 4 | 8 |
| 6[c] | **1a** (5) | DCB, CB | 4 | 3 | 0 |
| 7[d] | **1a** (5) | DCB, CB | 17 | 4 | Trace |
| 8 | **1a** (7.5) | DCB, CB | 50 | 18 | 2 |
| 9 | **1a** (10) | DCB, CB | 29 | 4 | 2 |
| 10 | **1a** (15) | DCB, CB | 9 | 4 | 3 |
| 11 | **1a** (5), CTAB (1) | DCB, CB | 63 | 8 | 0 |
| 12 | **1a** (5), CTAB (5) | DCB, CB | 19 | 11 | 0 |
| 13 | **1a** (5), CTAB (10) | DCB, CB | 6 | 4 | 5 |

[a] [DCB] = 3 mM, [CB] = 30 mM, [1-methylnaphthalene] = 5 mM.

[b] Isolated yields.

[c] In $H_2O/CH_3CN$ = 1:9.

[d] Under no stirring.



**Scheme 2.**

the photogenerated cation radicals (the cation radicals of **2** and the naphthyl moiety of **1b**) react with the carboxylate anion to give the decarboxylated product.[11] Although a similar photochemical decarboxylation of the carboxylate anion via electron transfer has already been reported,[12] the reaction between a cation radical and a carboxylate anion has not been investigated. A detailed study of this mechanism and the development of this type of photoreaction are now in progress in this laboratory and will be reported in separate publications.

These results may be rationalized as follows. The cation radical of the naphthyl moiety of **1a** and the anion radical of DCB are formed via the electron transfer between the excited **1a** and DCB in the oil droplet. The cation radical of **1a** is reduced by the indene **2** to produce the cation radical of **2**; on the addition of water, this radical gives alcohol **3** at the interface (Fig. 2, **A**). The decrease in the oil droplet size on the addition of CTAB improved the yield of **3** due to an increase in the oil–water surface area (Fig. 2, **B**). However, in the presence of a higher concentration of the cationic surfactant, the influence of the cationic charge increases by further decreasing the droplet size. In this case, the formation of the cation radicals might be prevented by the surfactant charge and results in a lower yield of **3** (Fig. 2, **C**). On the other hand, the use of the anionic surfactant **1b** quenches the photogenerated cation radicals at the interface, and the formation of alcohol **3** is also retarded. The formation of the decarboxylated product **6** indicates that the electron transfer from the carboxylate anion of **1b** to the cation radicals takes place at the interface. It is evident from these results that the highest yield of **3** is achieved when an appropriate oil droplet size is attained in the presence of the cationic surfactant.

In conclusion, we found that the redox-photosensitized reaction of indene proceeds efficiently by using the photosensitive surfactant **1a** in a microheterogeneous system to yield alcohol **3** as a major product and is strongly influenced by the droplet size and the surfactant charge. The selectivity and efficiency of a photoinduced electron transfer reaction in an emulsion can be controlled through the droplet size and ionic surfactant; thus, photoreactions using photosensitive surfactants in emulsions can be used as a new synthetic method.

## Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (No. 15750081) from the Japan Society of Promotion of Science. We thank Professor Isa and Dr. Sugihara, University of Fukui, for helpful discussions.

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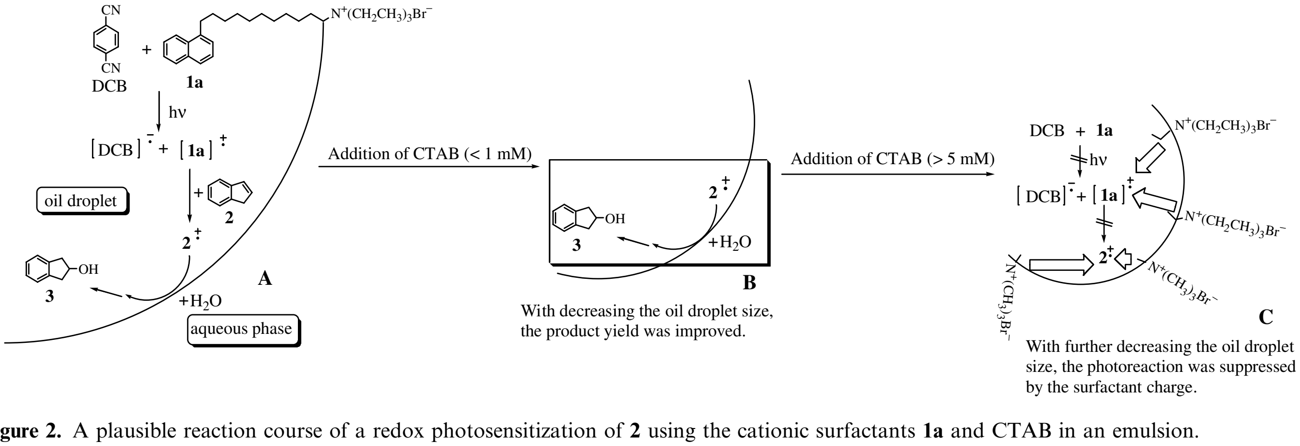

**Figure 2.** A plausible reaction course of a redox photosensitization of **2** using the cationic surfactants **1a** and CTAB in an emulsion.

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6. Spectra data for **1a**; mp 108 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$ 8.04 (d, 1H, $J = 8.5$ Hz), 7.84 (d, 1H, $J = 8.1$ Hz), 7.69 (d, 1H, $J = 7.9$ Hz), 7.51–7.37 (m, 3H), 7.31 (d, 1H, $J = 6.1$ Hz), 3.50 (q, 6H, $J = 7.3$ Hz), 3.25 (t, 2H, $J = 8.6$ Hz), 3.06 (t, 2H, $J = 7.9$ Hz), 1.77–1.67 (m, 4H), 1.46–1.26 (m, 23H); $^{13}$C NMR (125 MHz, $D_2O$) $\delta$ 139.3, 134.7, 132.6, 129.6, 127.3, 126.6, 126.5, 126.4, 126.3, 124.5, 57.2, 53.5, 33.7, 31.5, 30.5, 30.5, 30.4, 30.3, 30.2, 29.7, 26.8, 22.0, 7.8; MS(FAB) 383 ($M^{+}-Br$); Anal. Calcd for $C_{27}H_{37}NBr$: C, 70.11; H, 9.59; N, 3.03. Found: C, 70.40; H, 9.60; N, 3.26.
7. After the photoreaction, the emulsion was added to a 10% aqueous NaOH solution. The mixture was extracted with ether and ethyl acetate to give the products, CB and DCB, and bring about the recovery of **1a** (93%).
8. This measurement was performed by using the super dynamic light scattering spectrophotometer (DLS-7000, Otsuka Electronics Co., Ltd).
9. These droplet sizes could not be measured by dynamic light scattering since very little light was scattered.
10. When the basic aqueous solution (NaOH, 25 mM) including CB, DCB, and 1-methylnaphthalene (30, 3, and 5 mM, respectively) was irradiated, the product yields were the same as those mentioned in entry 3 in Table 1. This result indicates that the efficiency of this photoreaction does not differ if the pH range is changed.
11. The intramolecular electron transfer between the excited naphthyl moiety and the carboxylate anion of **1b** did not occur; the fluorescence spectrum of **1b** ($6 \times 10^{-4}$ M) in the aqueous NaOH (25 mM) solution was very close to that in the acetonitrile solution. Thus, the photogenerated cation radicals might be quenched by the anionic surfactant at the interface.
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