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Novel Photorearrangement of *N*-(1-Naphthoyl)-*N*-phenyl-*O*-benzoylhydroxylamine in Micellar Media

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Abstract: Analysis of the effects of added benzyl alcohol and a heavy atom (Br^-) on the quantum yields for the benzophenone-sensitized reaction of the title hydroxylamine in hexadecyltrimethylammonium chloride micelles revealed that the benzoyloxy-migrated products are derived from the amidyl-benzoyloxyl radical pair that is present at the micellar surface, whereas the amidyl-phenyl radical pair that is penetrated more deeply into the micellar interior is responsible for the appearance of the phenyl-rearranged products.
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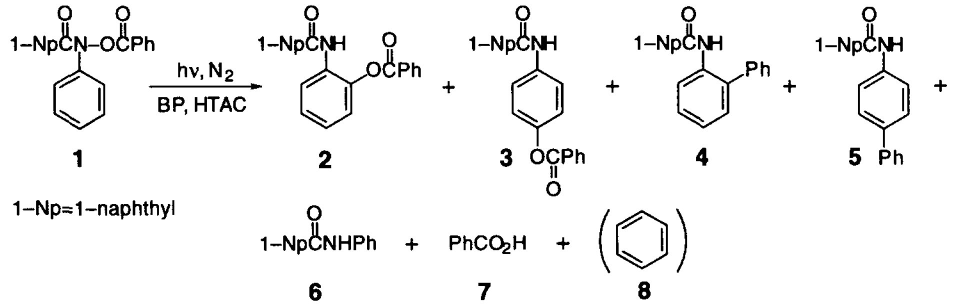
It is well known that micelle is a good device for inducing an efficient cage reaction of a triplet radical pair (which is produced photochemically) as a result of a significant decrease in the rate of escape of the radical pair from the micelle cage.[1] *N,O*-Diacyl-*N*-phenylhydroxylamines in the excited triplet state were shown to give only fragmentation products without undergoing any acyloxy migration.[2] Additionally, quantitative analysis of solvent effects on the intramolecular triplet-sensitized photolysis of diacylhydroxylamines with the benzophenone moiety confirmed that the decarboxylation of the aroyloxyl radical occurs from the vibrationally excited (hot) triplet radical pair, deactivation of which is markedly promoted by forming hydrogen bonds to protic solvents.[3] Thus, we are able to generate both the triplet aryl-amidyl and the aroyloxyl-amidyl radical pairs through the triplet-sensitized photolysis of the model diacylhydroxylamine in the micelle cage. This paper reports the novel photorearrangement of *N*-(1-naphthoyl)-*N*-phenyl-*O*-benzoylhydroxylamine (**1**) in hexadecyltrimethylammonium chloride (HTAC) micelles containing benzophenone (BP).



Scheme 1

On irradiation of a nitrogen-purged aqueous solution of **1** (1.0×10^{-3} mol dm^{-3}) with 366 nm light in the presence of BP (2.0×10^{-2} mol dm^{-3}) and HTAC (0.10 mol dm^{-3}: [micelle]= 8.7×10^{-4} mol dm^{-3})[4] at room

Table 1. Quantum yields for disappearance of **1** (Φ_{-1}) and for appearance of **2**–**7** (Φ_{2-7}) at 25±3°C

Solvent	Φ_{-1}	Φ_2	Φ_3	Φ_4	Φ_5	Φ_6	Φ_7
HTAC/H_2O[a]	0.300 ±0.012	0.100 ±0.007	0.051 ±0.006	0.024 ±0.002	0.020 ±0.002	0.093 ±0.006	0.081 ±0.007
MeOH[a]	0.302 ±0.012	0[c]	0	0	0	0.300 ±0.012	0.262 ±0.015
CH_2ClCH_2Cl[a]	0.647 ±0.042	0	0	0	0	0.623 ±0.035	0.139 ±0.011
HTAC/H_2O[b]	0.376 ±0.012	0.207 ±0.009	0.129 ±0.007	0	0	0	0

[a] BP-sensitized photolysis with 366 nm light. [b] Direct photolysis with 313 nm light. [c] Zero means $\Phi<0.001$.

temperature, six new HPLC signals were detected on the chromatogram, while the signal area of BP remained constant during the irradiation. Comparison of the HPLC behavior for the products with that for independently prepared authentic samples under various analytical conditions revealed that the BP-sensitized reaction of **1** in HTAC micelles results in the formation of the benzoyloxy-(**2** and **3**) and the phenyl-(**4** and **5**)migrated products along with the fragmentation **6** and **7** (Scheme 1). The fact that irradiation of a 1,2-dichloroethane or a methanol solution of **1** containing BP with 366 nm light under nitrogen gives only **6** and **7** demonstrates that the micelle cage exerts a dramatic effect upon the product distribution. In Table 1 are shown quantum yields (Φ) for the BP-sensitized reactions in HTAC micelles, 1,2-dichloroethane and methanol as well as for the direct photolysis with 313 nm light in this micellar phase.[5] The previous study[3] allows us to assume that the decarboxylation of the benzoyloxyl radical occurs from the hot triplet radical pair $^3[\text{1-NpC(=O)N(Ph)} \cdot\ \cdot \text{OC(=O)Ph}]^\ddagger$, hydrogen-bonding solvation of which promotes the deactivation of this pair to eventually afford **6** and **7** in quantum yields comparable to each other. Application of this assumption to the results obtained in 1,2-dichloroethane and methanol shows that the reaction in the former solvent proceeds mainly via the decarboxylation [benzene (**8**) could be detected by GLC] while the vibrationally relaxed radical pair predominantly participates in the reaction in the latter solvent. Thus, the observation of the larger Φ value for the formation of the benzoyloxyl radical-derived products ($\Phi_2 + \Phi_3 + \Phi_7 = 0.232$) than that of the phenyl radical-derived products ($\Phi_4 + \Phi_5 + \Phi_6 - \Phi_7 = 0.056$) in HTAC micelles substantiates the occurrence of the hydrogen-bonding solvation mentioned above. Both **1** and BP are deemed to be incorporated into the micellar surface.

It is very likely that the hot radical pair $^3[\text{1-NpC(=O)N(Ph)} \cdot\ \cdot \text{OC(=O)Ph}]^\ddagger$ simultaneously generates the amidyl-benzoyloxyl and the amidyl-phenyl radical pairs in the micelle cage.[3] The hydrophobicity of these radicals as well as the high intramicellar viscosity (18 mPa s at 30℃)[6] markedly reduces the rate of escape of the radical pairs from the micelle cage relative to the rate of intersystem crossing to the singlet pairs, thereby causing efficient geminate recombination which is responsible for the appearance of **2**–**5**. Inspection of Table 1 clearly indicates the exclusive formation of the 1,3-(**2**) and the 1,5-(**3**)benzoyloxy migrated products on irradiation of a micellar solution of **1** with 313 nm light. Elucidation of the origin of the fragmentation products **6** and **7** obtained in the HTAC micellar solution was an important issue. In order to determine whether these two fragments are formed in the micellar phase or in the aqueous phase, we examined the effects of added benzyl alcohol on the quantum yields (Figure 1). Since this hydrophobic alcohol should be largely accommodated into

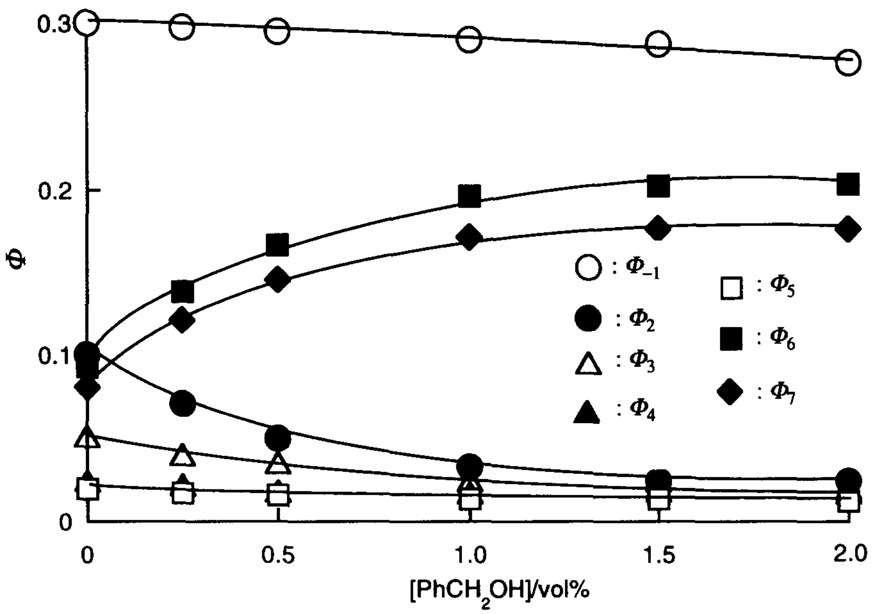
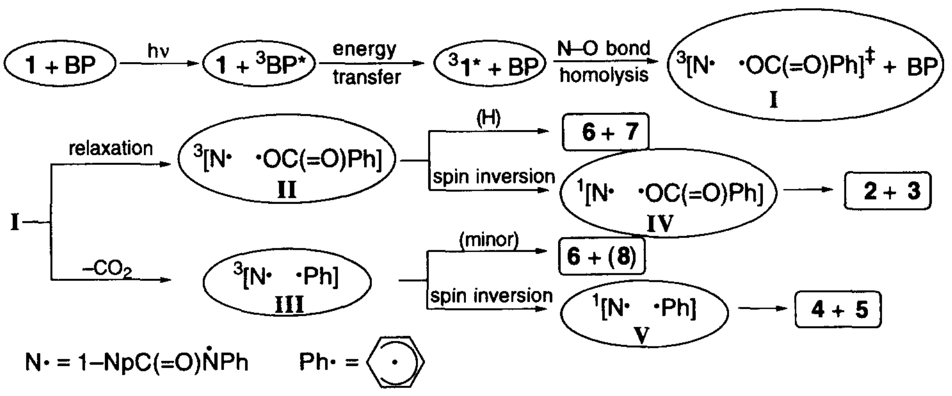


Figure 1. Effects of added benzyl alcohol on the quantum yields (Φ) for the **1**-BP-HTAC system.

the micellar aggregate and, in addition, the direct photolysis of **1** in HTAC micelles (which affords a singlet radical pair exclusively,[2]) gives only the rearrangement products **2** and **3**, the fact that an increase in the alcohol concentration enhances Φ_6 and Φ_7 accompanied by a decrease in Φ_2 and Φ_3 leads us to conclude that the hydrogen abstraction of the amidyl and benzoyloxyl radicals takes place in competition with the spin inversion of these triplet radicals in the micellar phase. The detection of benzaldehyde as the alcohol-derived product provides supporting evidence for this conclusion. Taking into account the fact that spin correlation is lost for caged radical pairs formed by re-encounter of free radicals,[7] we were led to propose Scheme 2 based on these considerations. The existence of benzyl alcohol in the micellar phase may not only increase the proportion of the solvent-separated radical pair relative to that of the contact radical pair but also accelerate the hydrogen abstraction within the former radical pair.



Scheme 2

As is shown in Figure 1, Φ_4 and Φ_5 are subject to the negligible effect of added benzyl alcohol. Since the alcohol is considered to exist at the micellar surface, this finding implies that the singlet radical pair **V** is more deeply buried in the micellar interior. Interestingly, the BP-sensitized reaction of **1** (1.0×10^{-3} mol dm^{-3}) in hexadecyltrimethylammonium bromide (HTAB, 0.10 mol dm^{-3}) micelles with 366 nm light produced only **4–7** without forming **2** and **3** ($\Phi_{-1} = 0.290 \pm 0.017$; $\Phi_4 = 0.050 \pm 0.004$; $\Phi_5 = 0.102 \pm 0.005$; $\Phi_6 = 0.126 \pm 0.010$; $\Phi_7 = 0.110 \pm 0.008$). It is known that the more hydrophobic Br^- (compared with Cl^-) decreases the water concentration at the micellar interface to greatly suppress water penetration into micelles[8] and also modifies singlet-triplet intersystem crossing efficiencies through its heavy-atom effect.[9] The former finding explains why the Φ_4 and Φ_5 values are increased by a factor of 2–5 for the reaction in HTAB micelles as compared to that in HTAC. In other words, less effective hydrogen-bonding solvation of the hot radical pair **I** in the HTAB micellar surface results in a more efficient decarboxylation within **I** to eventually give **4** and **5** in larger quantum yields as observed (Scheme 2). If the intersystem crossing from **II** to **IV** undergoes heavy-atom effects, we expect to observe the increased Φ_2 and Φ_3 with the decreased Φ_6 and Φ_7, upon the sensitized photolysis in the HTAB micelle cage. Because the hydrogen abstraction in **II** (that yields **6** and **7**) may compete with the intersystem crossing to **IV**, the benzoyloxy-migrated products should be formed in negligible quantum yields, provided that the opposite process **IV**→**II** is subject to pronounced heavy-atom effects. The presence of Br^- at the interface is, therefore, concluded to accelerate the intersystem crossing **IV**→**II** to a much larger extent than its reverse process.[10] On the other hand, a similar heavy-atom effect was not observed for either Φ_4 or Φ_5, being consistent with deeper penetration of the radical pairs **III** and **V** into the micellar interior as already mentioned.

In conclusion, we have demonstrated here that by utilizing micelle supercages and their counterions one can dramatically alter the product distribution that is obtained by the BP-sensitized reaction of **1** in homogeneous solutions.

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10. The direct photolysis of **1** in HTAB micelles gave measurable amounts of the fragmentation products **6** and **7** in addition to the rearranged products **2–5** ($\Phi_{-1} = 0.277 \pm 0.008$; $\Phi_2 = 0.126 \pm 0.005$; $\Phi_3 = 0.060 \pm 0.003$; $\Phi_4 = 0.015 \pm 0.001$; $\Phi_5 = 0.012 \pm 0.001$; $\Phi_6 = 0.034 \pm 0.004$; $\Phi_7 = 0.030 \pm 0.004$). This result is consistent with our conclusion. From these quantum yields it is suggested that both the excited singlet-state **1** and the singlet radical pair (which is produced by the direct photolysis) are subject to heavy-atom effects. A detailed discussion of the heavy-atom effect on the quantum yields will be given elesewhere.

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