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Benzophenone-Sensitized Photolysis of *N*,*N*-Dibenzyl-*O*-acylhydroxylamines. Mechanism of the Imine-Forming Radical Elimination Reaction

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Title hydroxylamines (**1**) undergo benzophenone-sensitized photolysis to give *N*-benzylidenebenzylamine (**2**), *p*-substituted benzoic acids (**3**), and monosubstituted benzenes (**4**) derived from decarboxylation of *p*-substituted benzoyloxyl radicals. Analysis of the linear Stern–Volmer plots, both for the sensitized photolysis of **1** and for the phosphorescence quenching of benzophenone by **1**, demonstrates the participation of triplet **1** in this photolysis. The logarithm of the ratio (k_r/k_d), where k_r is the rate constant for homolytic cleavage of the N–O bond in triplet **1** and k_d is that for its deactivation, used as a measure of the triplet-state reactivities of **1**, exhibited a good Hammett-type relationship against the substituent constant (σ) with a slope (ρ) of -0.75. This indicates the exclusive occurrence of homolysis of the N–O bond in the first excited triplet state of **1**. Thus the decomposition of **1** activated by triplet benzophenone is classified as an imine-forming radical elimination. The results of deuterium isotope and micellar effects on the sensitized photolysis suggest that the "out-of-cage" products **4** are obtained by decarboxylation and subsequent hydrogen abstraction of *p*-substituted benzoyloxyl radicals which escaped from the triplet cage in competition with spin inversion to the singlet cage. In this singlet cage, hydrogen abstraction giving **2** and **3** and recombination affording the starting **1** were found to take place exclusively.

Much effort has been devoted to synthetic, mechanistic, and theoretical studies on olefin-forming eliminations and has contributed to the establishment of one of the chemical paradises.[1] A detailed mechanistic investigation of these unimolecular and bimolecular eliminations has unraveled the delicate transition-state structure for the reactions.[2] Base-promoted imine-forming eliminations have recently been found[3] and a detailed comparison has been made between mechanisms of olefin- and imine-forming eliminations, with attention focusing primarily upon the effects of the nitrogen atom in a molecule on the transition-state structure.[4] On the other hand, there are some interesting reports describing the stereochemistry of olefin-forming radical eliminations.[5]

In contrast with ionic imine-forming eliminations there has been no study on imine-forming radical eliminations as far as we know. As an extension of our systematic study of the direct and sensitized photolyses of hydroxamic acid derivatives,[6a-e] we prepared *N*,*N*-dibenzyl-*O*-acylhydroxylamines (**1a**—**c**) and investigated benzophenone (BP)-sensitized photolysis of these compounds, hoping to find an imine-forming radical elimination and to gain an insight into its mechanism. In this paper we present the first observation of imine-forming radical eliminations of **1a**—**c** and discuss their mechanism.

$(PhCH_2)_2N{-}OC(=O)C_6H_4R\text{-}p$

1a: R= OMe 1b: R= F 1c: R= CF_3

Results

Products Derived from the Sensitized Photolysis. An oxygen-free acetonitrile solution of **1a** (0.020 M, 1 M=1 mol dm^{-3}) containing BP (0.020 M) was irradiated for a given period of time with light of wavelengths longer than 320 nm on a merry-go-round irradiation apparatus. The products were identified by comparing their HPLC or GLC behavior with that of commercially available authentic samples. As shown in Fig. 1, *N*-benzylidenebenzylamine (**2**), *p*-anisic acid (**3a**), and anisole (**4a**, data

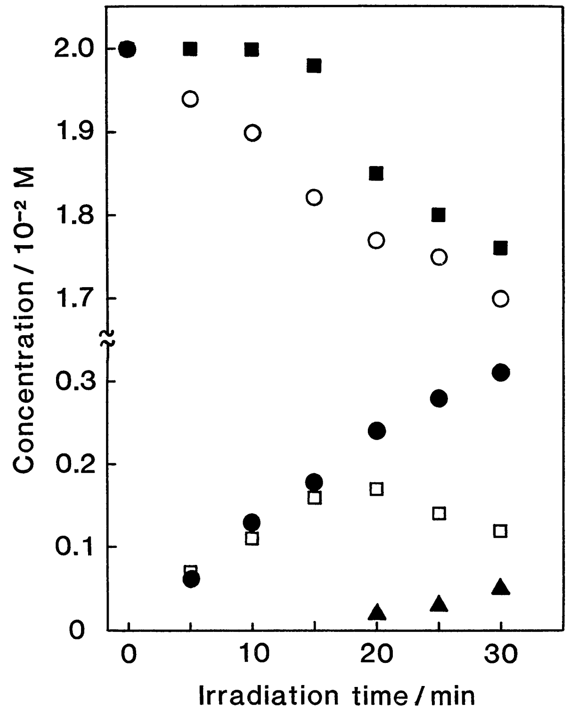


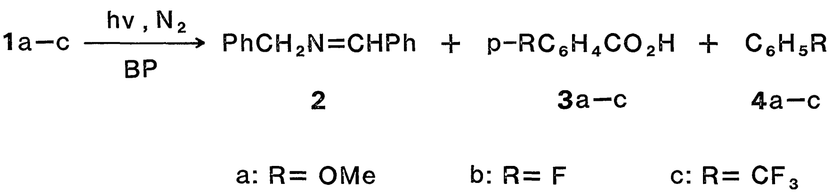
Fig. 1. Plots of reactant and product concentrations against irradiation time for the BP (0.020 M)-sensitized photolysis of **1a** (0.020 M) with light of wavelengths longer than 320 nm in oxygen-free acetonitrile. ○: **1a**, ●: **3a**, □: **2**, ■: BP, ▲: benzopinacol.

not presented) were obtained as the only detectable products at conversions lower than 9%, while BP remained unchanged during the irradiation. On the other hand, a secondary photoreaction between **2** and BP in excited states occurred to give benzopinacol as one of the products at conversions higher than 12%. This secondary photoreaction is reflected in a decrease in both **2** and BP concentrations (Fig. 1) and was confirmed by independent irradiation of **2** in the presence of BP under identical conditions. Control experiments revealed that there was no decomposition of **1a** without BP under the same irradiation conditions. The detectable formation of **4a**, derived from decarboxylation of *p*-anisoyloxyl radical, suggests the involvement of homolytic cleavage of the N-O bond in **1a**. Similar results were obtained by BP-sensitized photolysis of **1b** and **1c** (Scheme 1).

Quenching of the BP Phosphorescence by 1a—c. The room-temperature phosphorescence of BP (the first triplet excitation energy, E_{T_1}=69 kcal mol^{-1}; 1 kcal= 4.184 kJ)[7] was quenched by **1a**—**c** according to the Stern-Volmer equation (Fig. 2). The E_{T_1} values of **1a**—**c** (69, 67, and 67 kcal mol^{-1} for **1a**, **1b**, and **1c**, respectively) were estimated from the 0-0 peaks of their phosphorescence spectra in methanol-ethanol (1:1 v/v) at 77 K. Although the fluorescence of **1a**—**c** is too weak to be detected, it is evident from a comparison of the UV spectra of **1a**—**c** with that of BP that the first singlet excitation energy of **1a**—**c** is much higher than that of BP. Thus the BP-phosphorescence quenching is due to triplet-triplet energy transfer from BP to **1a**—**c** but not due to singlet-singlet energy transfer. The quenching constants ($k_t\tau_T$, where k_t and τ_T refer to the rate constant for triplet-triplet energy transfer and the lifetime of triplet BP without **1a**—**c**, respectively) were determined from the slopes of linear Stern-Volmer plots (Fig. 2) to be 62, 48, and 56 M^{-1} for **1a**, **1b**, and **1c**, respectively. A comparison of these constants demonstrates that the triplet energy transfer efficiency undergoes substituent effects, if any, to only a small extent.

Quantum Yields for the Sensitized Photolysis. The results of BP-phosphorescence quenching as well as product analysis suggest that the BP-sensitized photolyses of **1a**—**c** proceed according to Scheme 2 which allows us to derive Eqs. 1 and 2 under the steady-state approximation:

$$1/\Phi_{-1}=1/\Phi_2=(1+k_d/k_r)(1+1/k_t\tau_T[\mathbf{1a}\text{—}\mathbf{c}]) \qquad (1)$$



$$\mathbf{1a\text{-}c} \xrightarrow[\text{BP}]{h\nu,\ N_2} \underset{\mathbf{2}}{PhCH_2N{=}CHPh} + \underset{\mathbf{3a\text{-}c}}{p\text{-}RC_6H_4CO_2H} + \underset{\mathbf{4a\text{-}c}}{C_6H_5R}$$

a: R= OMe b: R= F c: R= CF$_3$

Scheme 1.

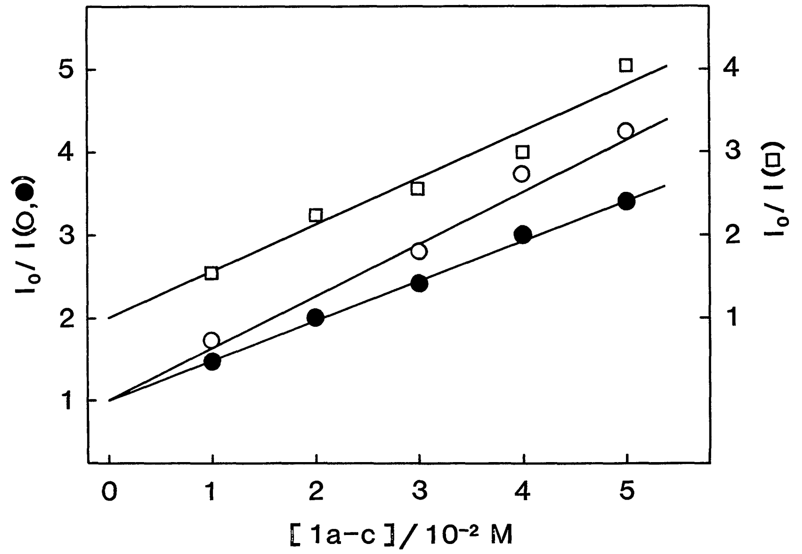


Fig. 2. Stern-Volmer plots for the quenching of BP (0.050 M) phosphorescence by **1a** (○), **1b** (●), and **1c** (□) under nitrogen in acetonitrile at room temperature (26±1 °C). I and I_0 are the phosphorescence intensity of BP with and without **1a**—**c**, respectively.

	Process (rate constant)
$\mathrm{BP(S_0)} \xrightarrow{h\nu} \mathrm{BP(S_1)} \xrightarrow{\Phi\mathrm{isc}=1} \mathrm{BP(T_1)}$	Absorption of light and intersystem crossing
$\mathrm{BP(T_1)} \xrightarrow{kd'=1/\tau_T} \mathrm{BP(S_0)}$	Deactivation of triplet BP (kd')
$\mathrm{BP(T_1)} + \mathrm{1a\text{–}c(S_0)} \xrightarrow{kt} \mathrm{BP(S_0)} + \mathrm{1a\text{–}c(T_1)}$	Triplet-triplet energy transfer (kt)
$\mathrm{1a\text{–}c(T_1)} \xrightarrow{kd} \mathrm{1a\text{–}c(S_0)}$	Deactivation of triplet 1a–c (kd)
$\mathrm{1a\text{–}c(T_1)} \xrightarrow{kr} \underset{\mathrm{I\cdot}}{\mathrm{(PhCH_2)_2N\cdot}} + \underset{\mathrm{IIa\text{–}c\cdot}}{\mathrm{ArCOO\cdot}}$	Homolytic cleavage of the N-O bond (kr)
$\mathrm{I\cdot} + \mathrm{IIa\text{–}c\cdot} \xrightarrow{k_1} 2 + \mathrm{3a\text{–}c}$	Hydrogen abstraction (k_1)
$\mathrm{I\cdot} + \mathrm{IIa\text{–}c\cdot} \xrightarrow{k_2} 2 + \mathrm{4a\text{–}c} + \mathrm{CO_2}$	Decarboxylation and hydrogen abstraction (k_2)

Scheme 2.

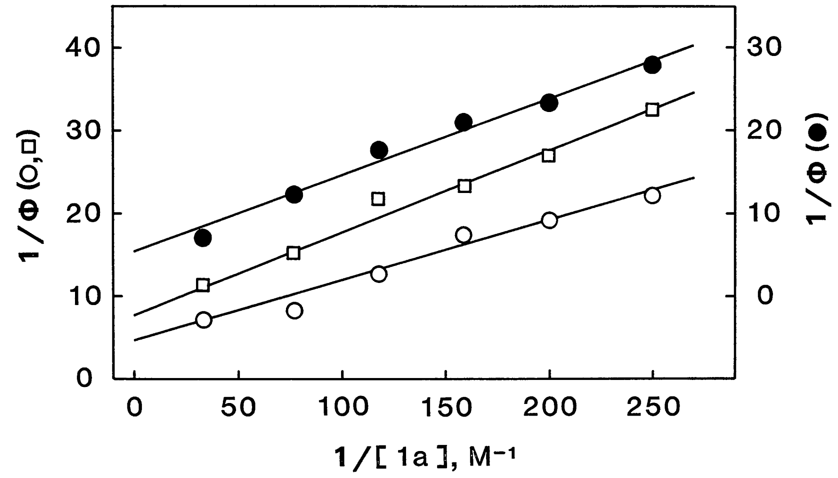


Fig. 3. Stern-Volmer plots of $1/\Phi_{-1a}$ (○), $1/\Phi_2$ (●), and $1/\Phi_{3a}$ (□) versus 1/[**1a**] for the BP (0.050 M)-sensitized photolysis of **1a** with 366-nm light in oxygen-free acetonitrile.

$$1/\Phi_3=(1+k_d/k_r)(1+k_2/k_1)(1+1/k_t\tau_T[\mathbf{1a—c}]) \tag{2}$$

where Φ_{-1}, Φ_2, and Φ_3 are the quantum yields for the disappearance of **1a**—**c** and for the appearance of **2** and **3**, respectively. These quantum yields were determined by using a potassium trioxalatoferrate (III) actinometer at low conversions (3—4%) of the starting **1a**—**c**. If our Scheme for the sensitized photolysis is valid, then we expect a linear relationship between $1/\Phi$ and the reciprocal of **1a**—**c** concentrations (1/[**1a**—**c**]). In Fig. 3 are shown typical double reciprocal plots for the BP-sensitized photolysis of **1a** in acetonitrile. Similar plots were obtained also for **1b** and **1c**.

The good linear correlation between $1/\Phi$ and 1/[**1a**—**c**], therefore, justifies the validity of Scheme 2. These linear Stern-Volmer plots of $1/\Phi_{-1}$, $1/\Phi_2$, and $1/\Phi_3$ vs. 1/[**1a**—**c**] allow us to estimate the limiting quantum yields for the disappearance of **1a**—**c** ($\Phi_{-1,\mathrm{lim}}$) and for the appearance of **2** ($\Phi_{2,\mathrm{lim}}$) and **3a**—**c** ($\Phi_{3,\mathrm{lim}}$). In addition, the intercept/slope ratios of these linear plots provide the $k_t\tau_T$ values, while the k_r/k_d values can be evaluated based on Eq. 1. All of these values (Φ_{lim}, $k_t\tau_T$, and k_r/k_d) are

Table 1. Limiting Quantum Yields and Related Parameters for the BP (0.050 M)-Sensitized Photolysis of **1a—c** (0.0040—0.030 M) with 366-nm Light under Nitrogen at 28±2°C

Compound	Solvent	$\Phi_{-1,\mathrm{lim}}$	$\Phi_{2,\mathrm{lim}}$	$\Phi_{3,\mathrm{lim}}$	Φ_4	$\Phi_{4,\mathrm{lim}}$[a]	k_r/k_d	$k_t\tau_T$[b] / M^{-1}	$k_t\tau_T$[c] / M^{-1}
1a	CH_3CN	0.22	0.19	0.13	0.03[d]	0.08	0.26	62	67
1b	CH_3CN	0.13	0.12	0.10	—[e]	0.03	0.14	48	49
1c	CH_3CN	0.06	0.06	0.03	—[e]	0.03	0.064	56	90
1a-*d*₄	CH_3CN	0.11	0.10	0.07	—[f]	0.04	0.12	60	63
1a	CH_2ClCH_2Cl	0.22	0.23	0.18	—[f]	0.05	0.29	56	53
1a	Benzene	0.28	0.29	0.29	≈0[d]	0	0.40	36	27

a) Calculated by assuming $\Phi_{4,\mathrm{lim}}=1/2(\Phi_{-1,\mathrm{lim}}+\Phi_{2,\mathrm{lim}})-\Phi_{3,\mathrm{lim}}$. b) Determined from the BP-phosphorescence quenching experiments. c) Average of the $k_t\tau_T$ values determined from the quantum yield (Φ_{-1}, Φ_2, and Φ_3) measurements. d) Determined for [**1a**]=0.030 M (GLC analysis). e) Could not be determined. f) Not determined.

collected in Table 1 which also includes the results of solvent and deuterium isotope effects on the quantum yields for the BP-sensitized photolysis of **1a**. The latter effects were examined in acetonitrile by use of *N*,*N*-di(benzyl-α-d_2)-*O*-(*p*-anisoyl)hydroxylamine (**1a-*d*₄**). An additional supporting evidence for Scheme 2 comes from the finding that the $k_t\tau_T$ value determined from the BP-phosphorescence quenching corresponds well to that obtained from the linear plot of $1/\Phi$ against $1/[\mathbf{1}]$ for any starting **1** as well as in any solvent studied.

Discussion

Substituent and Deuterium Isotope Effects. Because the $k_t\tau_T$ values obtained for **1a**, **1b**, and **1c** in acetonitrile may be taken as consistent with each other within the experimental error, we can discuss a difference in the reactivity among these compounds from the standpoint of substituent effects on the triplet-state reactivities (k_r/k_d). One expects that an increased electron-withdrawing ability of the substituent R should accelerate heterolytic cleavage of the N-O bond in **1**[3] whereas it may suppress homolytic cleavage of this bond because of an electrophilic character of the aroyloxyl radical formed by this type of N-O bond cleavage.[8] A comparison of the k_r/k_d values obtained for **1a**—**c** in acetonitrile establishes that the triplet-state reactivity decreases with increasing electron-withdrawing ability of the substituent R; this strongly evidences that homolytic cleavage of the N-O bond occurs in triplet **1a**—**c**. An important problem is whether the substituent R affects the triplet-state deactivation (k_d) or the N-O bond cleavage (k_r) process. Figure 4 shows that there is a nice Hammett-type linear relationship with a slope (ρ) of −0.75 between log (k_r/k_d) and the substituent constant σ values. This ρ value suggests a relatively large contribution of the ionic structure to the transition-state structure **III** for homolytic N-O bond cleavage in triplet **1a**—**c**.

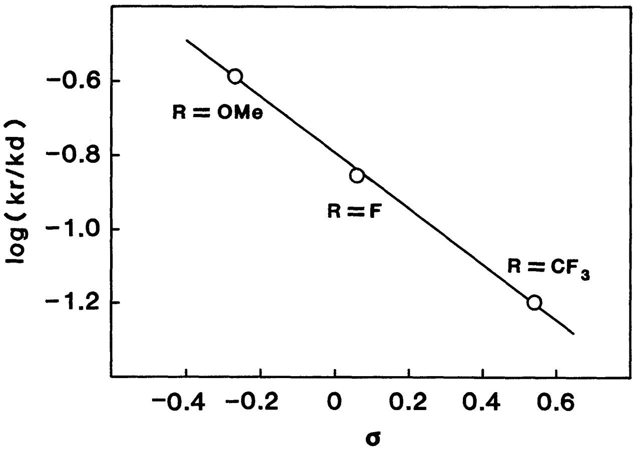


Fig. 4. Correlation of log (k_r/k_d) and σ values for the BP-sensitized photolysis of **1a—c** with 366-nm light in acetonitrile.

On the other hand, the Hammett ρ-σ correlation has been applied in order to scrutinize the transition-state structure for the homolysis of the benzylic C-H bond. The ρ values in a range of −0.4 to −1.0 have been obtained from this correlation depending on the structures of both substrates and attacking radicals, and explained in terms of a similar transition-state structure.[9] Thus the fact that our ρ value is comparable to these ρ values suggests that the N-O bond cleavage process rather than the triplet-state deactivation is mainly subject to polar substituent effects.

Inspection of Scheme 2 provides us another important problem: Is the benzylic hydrogen atom of dibenzylaminyl radical (I·) abstracted by aroyloxyl radical (II·)? To solve this problem we prepared **1a-*d*₄** and examined

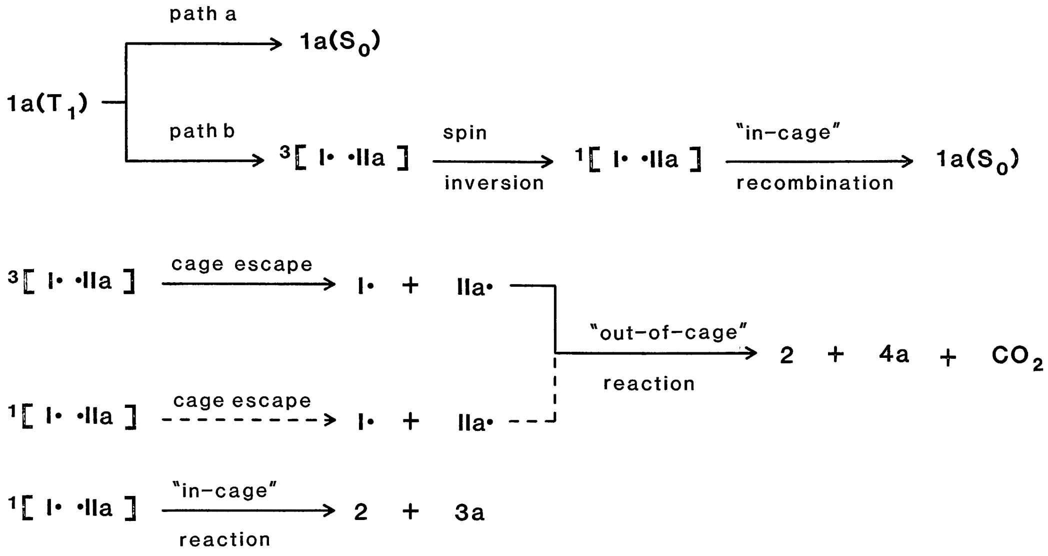
$$^3[\,\mathrm{Bzl_2}\overset{\delta\bullet}{\mathrm{N}}\text{----}\overset{\delta\bullet}{\mathrm{O}}\mathrm{C(=O)Ar} \longleftrightarrow \mathrm{Bzl_2}\overset{\delta-}{\mathrm{N}}\text{----}\overset{\delta+}{\mathrm{O}}\mathrm{C(=O)Ar}\,]^{\neq}$$

III

Bzl= $PhCH_2$ Ar= p-RC_6H_4

$(PhCD_2)_2N{-}OC(=O)C_6H_4OMe$-p

1a-d_4



Scheme 3.

deuterium isotope effects on the reaction of **1a** with triplet BP. The deuterium substitution decreases both the $\Phi_{\rm lim}$ and k_r/k_d values by a factor of about 2, whereas the $k_t\tau_T$ value is not affected by deuteration (Table 1). In order to discuss the mechanism of our imine-forming radical eliminations in more detail, we present Scheme 3 which takes into account the spin-correlated (singlet or triplet) radical pair in a solvent cage as already successfully applied to the BP-sensitized photolysis of *N*-(1-naphthoyl)-*O*-(*p*-toluoyl)-*N*-phenylhydroxylamine (NT).[6b)] A comparison of Schemes 2 and 3 shows that the rate constants k_r and k_d in Scheme 2 correspond to the rate of the N–O bond cleavage in triplet **1a**—**c** giving the triplet radical pair and to the total rate of physical (path a) and chemical (path b) deactivations of triplet **1a**—**c** affording eventually the starting **1a**—**c**, respectively. In addition, the rate constants k_1 and k_2 in Scheme 2 conform to the total rate of triplet→singlet cage spin inversion and subsequent "in-cage" hydrogen abstraction yielding **2** and **3a**—**c** and to the total rate of diffusive escape from the triplet cage, decarboxylation of "out-of-cage" aroyloxyl radicals, and subsequent hydrogen abstraction forming eventually **2**, **4a**—**c**, and CO_2, respectively.

The observation that the relative phosphorescence quantum yield $[\Phi_p(\mathbf{1a})/\Phi_p(\mathbf{1a}\text{-}d_4)]$ of **1a** and **1a-*d*₄** (E_{T_1}= 69 kcal mol^{-1}) at 77 K is nearly equal to unity makes it reasonable to assume that in addition to the N–O bond cleavage process of triplet **1a**, its physical deactivation process (path a in Scheme 3) also undergoes deuterium isotope effects to a negligible extent. Thus a decrease in $\Phi_{\rm lim}$ as well as k_r/k_d observed by deuteration implies that hydrogen abstraction from **I•** by **IIa•** takes place in competition with recombination of these two radicals to generate the starting **1a**. The latter process (path b in Scheme 3) contributes to accelerating the deactivation process of triplet **1a** and, hence, the deuteration of **1a** should enhance the chemical deactivation process of this triplet to reduce k_r/k_d as observed. In view of the fact that hydrogen abstraction to give **2** and **3a**—**c** (k_1 in Scheme 2) competes with decarboxylation to form eventually **2** and **4a**—**c** (k_2 in Scheme 2), the retardation of hydrogen abstraction by the deuterium incorporation is expected to be reflected in an increase in the relative rate of this decarboxylation and, thus, in the enhanced k_2/k_1 value. From Eqs. 1 and 2 we can estimate the k_2/k_1 values using the $\Phi_{\rm lim}$ values listed in Table 1: k_2/k_1 =0.57 (**1a**), 0.49 (**1a-*d*₄**), 0.25 (**1b**), and 1.0 (**1c**) in acetonitrile. A comparison of these values for **1a** and **1a-*d*₄** clearly indicates that decarboxylation of **IIa•** cannot compete with hydrogen abstraction from **I•** by this radical. This means that diffusive separation of **I•** and **IIa•** from the caged singlet radical pair must be slow enough to allow the exclusive hydrogen abstraction and recombination in this cage (Scheme 3). It is thus very likely that anisole (**4a**), one of the "out-of-cage" products, originates from decarboxylation of **IIa•** which escaped from the triplet cage in competition with spin inversion from the triplet to the singlet pair. Because diffusive separation of the caged radical pair is thought to undergo negligible deuterium isotope and polar substituent effects, our k_2/k_1 value may reflect the relative ease of this spin inversion, which is in the following order: R=F (k_2/k_1=0.25)>R=OMe (0.57)>R=CF_3 (1.0). Although this order seems to be consistent with that of the magnitude of heavy-atom effects of these substituents on the rate of spin inversion, we cannot discuss it in detail at the present stage.

Solvent and Micellar Effects. Our previous study on the BP-sensitized photolysis of NT indicated that the triplet-state reactivity (k_r/k_d) of this diacylhydroxylamine increases with decreasing solvent polarity.[6a,b)] On the other hand, a study of the micellar effects on the photolysis of NT provided us an interesting result that the "out-of-cage" reaction of the resulting radicals is almost completely suppressed in the micelle cage.[6b)] In order to discuss further the reaction course of imine-forming radical eliminations, we examined solvent and micellar effects on the BP-sensitized photolysis of **1a** chosen for this purpose.

The $k_t\tau_T$ values obtained by the above-mentioned two methods are in good agreement with each other also for 1,2-dichloroethane and benzene (Table 1), indicating that the reaction proceeds according to Scheme 2 in any solvent employed. In addition the triplet-state reactivity tends to increase with decreasing solvent polarity, although this reactivity is little affected by a change in solvent polarity. Interestingly the sensitized photolysis of **1a** in benzene does not give any **4a** derived from decarboxylation of **IIa·**. Because benzene is not so viscous (viscosity at 30 °C=0.5621 cP),[10)] it is very unlikely that only the "in-cage" reaction occurs in this nonpolar solvent. Ingold and co-workers have recently reported that in a nonpolar solvent, carbon tetrachloride, the rates of unimolecular decarboxylation and bimolecular hydrogen abstraction of **IIa·** increase by a factor of about 20 and 2—3, respectively, compared with those in a polar solvent, acetonitrile.[11)] Their results suggest that the reactivities of **IIa·** should increase to more extent in the nonpolar solvent, benzene, than in acetonitrile, and thus allow us to expect that we obtain a larger $\Phi_{4,\mathrm{lim}}$ value in benzene than in acetonitrile since solvent changes can have a dramatic effect on the rate of decarboxylation of **IIa·**. However, the result (Table 1) is not in line with this expectation. Aromatic solvents including benzene are known to form a charge-transfer-type π-complex with an electrophilic chlorine atom.[12)] The fact that aroyloxyl radicals add easily to alkenes suggests that these radicals also have an electrophilic character.[8)] Thus it is reasonable to assume that the radical **IIa·** forms a similar type of π-complex with benzene to stabilize this radical and, hence, to reduce the relative rate of decarboxylation of the "out-of-cage" radical **IIa·** to hydrogen abstraction from **I·** by **IIa·**. If benzene can enhance the reactivity of **I·** toward hydrogen abstraction to an extent similar to or more than that of **IIa·**, then the existence of such a π-complex provides a good explanation for the negligible formation of **4a** in benzene.

It is well established that micelles offer a large energy barrier to diffusive separation of a radical pair generated within the micellar phases, so that the efficiency of "in-cage" reaction of the triplet-derived radical pair is enhanced in a micellar solution to a larger extent than that in a homogeneous solution.[13)] Based on this characteristic of micelles we expect in the sensitized photolysis of **1a** in micelles that the quantum yield for the formation of **4a**, one of the "out-of-cage" products, becomes negligibly small.

The sensitized photolysis of **1a** (1.3×10^{-2} M) by BP (2.0×10^{-2} M) in hexadecyltrimethylammonium chloride (HTAC) micelles (1.8×10^{-3} M) under nitrogen at 28±1 °C gave the following results: $\Phi_{-1a}=0.03$, $\Phi_2=0.03$, $\Phi_{3a}=0.03$, and $\Phi_{4a}\approx0$. For comparison these quantum yields were determined in acetonitrile under identical conditions except for the omission of HTAC micelles: $\Phi_{-1a}=0.10$, $\Phi_2=0.09$, $\Phi_{3a}=0.08$, and $\Phi_{4a}=0.01$. The finding that the ratio ($I_0/I=1.9$) of BP-phosphorescence intensity with (I) and without (I_0) **1a** in micelles is consistent with that ($I_0/I=1.8$) obtained in acetonitrile under the same conditions allows us to discuss the differences in the quantum yields on the basis of micellar effects not on the triplet–triplet energy transfer efficiency but solely on the "in-cage" reaction efficiency. As we would expect, the formation of **4a** in HTAC micelles is negligible, whereas the quantum yields Φ_{-1a}, Φ_2, and Φ_{3a} for the reaction in this micelle decreased by a factor of about 3 compared with those in acetonitrile. Owing to the relatively large intramicellar viscosity of HTAC (18 cP at 30 °C),[14)] translational movement of the paired radicals **I·** and **IIa·** in this micelle should be restricted to a large extent to result in a more efficient recombination of **I·** and **IIa·** giving the starting **1a** than hydrogen abstraction from **I·** by **IIa·** forming **2** and **3a**, as observed. These observations, therefore, constitute further evidence for the occurrence of recombination in competition with hydrogen abstraction within the singlet solvent cage.

Experimental

General Methods. HPLC analysis of the photoproducts was performed on a Shimadzu Model LC-6A high-performance liquid chromatograph equipped with a 4.6×250-mm ODS (Zorbax) column and a Shimadzu Model SPD-2A UV detector (240 nm). IR spectra were taken with a Hitachi Model 270-30 infrared spectrometer. ^{1}H NMR spectra were recorded on a JEOL Model FX-200 spectrometer. GLC analysis was carried out on a Shimadzu Model GC-8AP gas chromatograph using a 3.0×3000-mm glass column packed with 10% Silicone SE-30 on Uniport B (60/80 mesh, Gasukuro Kogyo). Room-temperature phosphorescence of benzophenone with and without quencher was measured under nitrogen with a Shimadzu Model RF-5000 spectrofluorimeter. UV spectra at room temperature and phosphorescence spectra at 77 K were taken on a Shimadzu Model UV-210A spectrophotometer and a Shimadzu Model RF-500 spectrofluorimeter equipped with a cylindrical rotating sector, respectively.

Materials and Solvents. *N*,*N*-Dibenzylhydroxylamine was prepared according to the method of Jones and Sneed, mp 123—124 °C (lit,[15)] 124 °C). *O*-Aroylation of this hydroxylamine with *p*-substituted benzoyl chlorides in the presence of pyridine in dichloromethane gave *N*,*N*-dibenzyl-*O*-(*p*-substituted benzoyl)hydroxylamines in good yields. The crude products were purified by column chromatography over silica gel (70—230 mesh, Merck) using chloroform as eluent followed by repeated recrystallization from hexane to give colorless needles with the following physical properties.

N,*N*-Dibenzyl-*O*-(*p*-anisoyl)hydroxylamine (**1a**), mp 84.5—85.5 °C (lit,[3)] 83—84 °C); IR (KBr) 1730 cm^{-1} (ester C=O); ^{1}H NMR (CDCl$_3$) δ=3.83 (3H, s), 4.20 (4H, s), 6.87 (2H, d,

J=8 Hz), 7.24—7.48 (10H, m), and 7.82 (2H, d, J=8 Hz).

N,*N*-Dibenzyl-*O*-(*p*-fluorobenzoyl)hydroxylamine (**1b**), mp 99—100 °C; IR (KBr) 1740 cm^{-1} (ester C=O); ^{1}H NMR ($CDCl_3$) δ=4.20 (4H, s), 7.04 (2H, dd, J=8 and 8 Hz), 7.22—7.48 (10H, m), and 7.86 (2H, dd, J=8 and 5 Hz). Found: C, 75.32; H, 5.47; N, 4.16%. Calcd for $C_{21}H_{18}NO_2F$: C, 75.20; H, 5.41; N, 4.18%.

N,*N*-Dibenzyl-*O*-(*p*-trifluoromethylbenzoyl)hydroxylamine (**1c**), mp 98—99 °C; IR (KBr) 1745 cm^{-1} (ester C=O); ^{1}H NMR ($CDCl_3$) δ=4.22 (4H, s), 7.22—7.48 (10H, m), 7.59 (2H, d, J=8 Hz), and 7.91 (2H, d, J=8 Hz). Found: C, 68.59; H, 4.61; N, 3.69%. Calcd for $C_{22}H_{18}NO_3F_3$: C, 68.56; H, 4.71; N, 3.64%.

N,*N*-Di(benzyl-*α*-d_2)-*O*-(*p*-anisoyl)hydroxylamine (**1a**-d_4), mp 85—86 °C, was obtained from the reaction of *p*-anisoyl chloride with *N*,*N*-di(benzyl-*α*-d_2)hydroxylamine, which was prepared according to the previous method,[3] under the same conditions as those used for syntheses of **1a**—**c**. The content of deuterium in **1a**-d_4 was determined to be 98 atom% by ^{1}H NMR spectroscopy. Benzophenone was purified by repeated recrystallization from ethanol. Fractional distillation of *N*-benzylidenebenzylamine (**2**), anisole (**4a**), fluorobenzene (**4b**), and trifluoromethylbenzene (**4c**) gave analytically pure samples. *p*-Methoxy (**3a**)-, *p*-fluoro (**3b**)-, and *p*-trifluoromethyl (**3c**)-benzoic acids were recrystallized twice from aqueous ethanol. Benzene and 1,2-dichloroethane were of spectroscopic grade and were used without further purification. Purification of acetonitrile was done by standard methods. Hexadecyltrimethylammonium chloride (HTAC) was recrystallized twice from acetone–methanol and dried in vacuo.

Quantum Yields. A potassium trioxalatoferrate(III) actinometer[16] was employed to determine quantum yields for the benzophenone-sensitized photolysis at low conversions (3—4%) of the starting **1a**—**c**. A 450 W high-pressure Hg lamp was used as the light source from which 366-nm light for the photolysis was selected with Corning 0-52, Corning 7-37, and Toshiba IRA-25S glass filters. Linear calibration curves for each compound, made under the same analytical conditions, were utilized to quantify both the disappearance of **1a**—**c** and the appearance of **2** and **3a**—**c**. Quantum yields for the photolysis in HTAC micelles were determined similarly. All the quantum yields are average of more than six determinations. Quantitative GLC analysis of **4a** was done by using its calibration curve. Any attempt to separate the GLC peak of **4b** or **4c** from that of the solvent was unsuccessful so that quantum yields for these products could not be estimated.

The micelle concentration was evaluated on the basis of the equation [micelle]=([HTAC surfactant]−cmc)/N, where [HTAC surfactant]=0.20 M, critical micelle concentration, cmc=1.3×10^{-3} M, and aggregation number, N=113.[17] Both benzophenone and **1a** were stable in micellar solutions for a long period of time so that undesired dark reactions including hydrolysis of **1a** can be ignored during quantum yield determinations.

Parallel Irradiations. Ten milliliters of an acetonitrile solution of **1a**—**c** (0.020 M) and benzophenone (0.020 M) was placed in a Pyrex tube, degassed by bubbling oxygen-free nitrogen through it for 10 min, and sealed. The sealed tubes were irradiated in parallel for a given period of time on a merry-go-round apparatus (Riko Model RH400-10W) with a 400 W high-pressure Hg lamp through a Pyrex-cylindrical solution filter, which was an aqueous solution of Copper(II) sulfate pentahydrate (250 g dm^{-3}) and isolated light of wavelengths longer than 320 nm. All the irradiations were carried out in a water bath thermostated by circulating water.

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