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Imine-Forming Radical Elimination Reactions of *O*-(1-Naphthoyl)-*N*,*N*-bis(*p*-substituted benzyl)hydroxylamines Activated by Triplet Benzophenone

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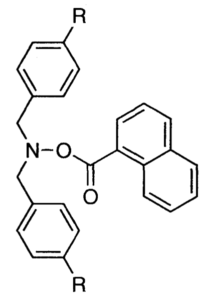
It was shown that despite the occurrence of a diffusion-limited triplet energy transfer between the title hydroxylamine **1** and benzophenone, triplet **1** decomposed inefficiently giving *p*-substituted *N*-(*p*-substituted benzylidene)benzylamine **2** and 1-naphthoic acid (**3**) as unimolecular radical elimination products. The logarithm of the k_r/k_d ratio (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**, showed a negligible dependence on the substituent constant. This finding was explained in terms of a very small contribution of the ionic structure to the transition state for the N–O bond homolysis.

Much effort has recently been devoted to mechanistic studies on imine-[1] and nitrile-[2] forming elimination reactions and has enabled the observation of important mechanistic differences between these reactions and alkene- and alkyne-forming eliminations.[3] In contrast with bimolecular and ionic imine-forming eliminations, there has been no study regarding imine-forming radical-elimination reactions. During the course of our systematic study of the direct and sensitized photolyses of *N*,*O*-diacyl-*N*-phenylhydroxylamines,[4] we found that the hydroxylamines readily undergo an N–O bond homolysis in the excited triplet state, giving aminyl and aroyloxyl radicals. If there exists hydrogen at the α position of the aminyl nitrogen atom, the aroyloxyl radical could abstract this hydrogen, yielding imine and carboxylic acid as unimolecular radical elimination products. From this point of view, we previously designed *O*-aroyl-*N*,*N*-dibenzylhydroxylamines and investigated the triplet-sensitized photolysis of these hydroxylamines, hoping to find a new type of imine-forming radical elimination. Analyses of substituent and deuterium isotope effects on the quantum yield for the reaction revealed that a caged singlet radical pair, in which hydrogen abstraction occurs affording elimination products (: imines and carboxylic acids), is involved in the reaction as a key intermediate.[5] It was previously found that the 1-naphthoyl group becomes a far more effective triplet-energy acceptor than the substituted benzoyl.[4] Since great difficulty may be experienced in introducing a series of substituents into the 4-position of the 1-naphthoyl chromophore, we designed *O*-(1-naphthoyl)-*N*,*N*-bis(*p*-substituted benzyl)hydroxylamines **1a**—**e** (Chart 1) in order to scrutinize the transition-state structure for the N–O bond cleavage through substituent effects on the benzophenone (BP)-sensitized photolysis of these hydroxylamines in acetonitrile (MeCN).



1a–e

R= Me (**1a**), H (**1b**), Cl (**1c**), Br (**1d**), CF_3 (**1e**)

Chart 1.

Results

Quenching of the BP Phosphorescence by 1a—e. As typically shown in Fig. 1, the room-temperature phosphorescence of BP (the first triplet excitation energy, E_T = 290 kJ mol^{-1}; the first singlet excitation energy, E_S = 311 kJ mol^{-1})[6] was quenched by **1a**—**e** according to the Stern–Volmer equation: $I_0/I = 1 + k_t\tau_T$ [**1**] in which I and I_0 are the emission intensities of BP with and without a given quencher, respectively. In Table 1 are collected the quenching constants [$k_t\tau_T$, where k_t and τ_T refer to the rate constant for energy transfer and the lifetime (26 μs)[7] of triplet BP without **1**, respectively] and k_t values. The E_T values of **1a**—**e** were estimated from the 0–0 peaks of their phosphorescence spectra in butyronitrile at 77 K, while the normalized UV absorption and fluorescence spectra made it possible for us to determine the approximate E_S values (Table 1). Because a singlet–singlet energy transfer from BP to any model hydroxylamines is highly endothermic, the ob-

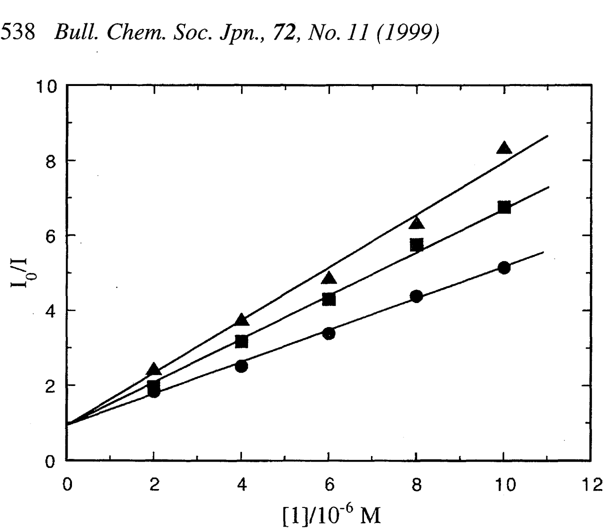


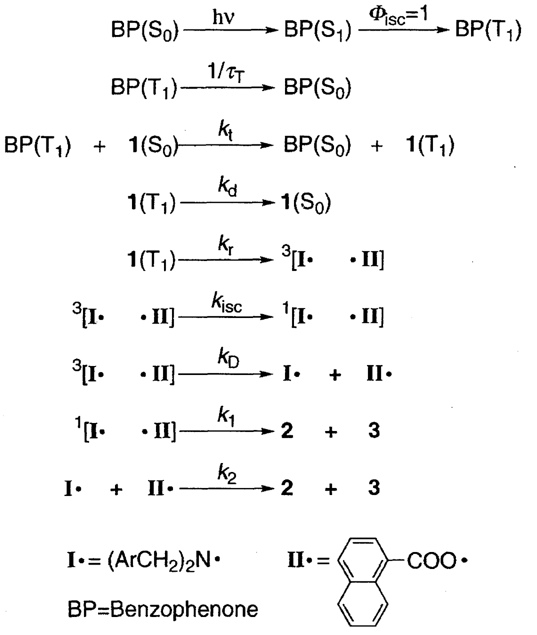
Fig. 1. Stern–Volmer Plots for the quenching of BP (0.030 M) phosphorescence by **1a** (●), **1b** (▲), and **1e** (■) in N_2-purged MeCN at room temperature. Excitation wavelength is 366 nm.

served phosphorescence quenching is due to an exothermic energy transfer between triplet BP and **1**. The magnitude of the rate constant for a triplet–triplet energy transfer clearly shows that the energy transfer takes place at the diffusion-limited rate without undergoing a significant substituent effect. It is worth noting that the energy-transfer efficiency for the present system is greater than that for the previously studied system by about four orders of magnitude.[5]

Quantum Yields for the Sensitized Photolysis. The irradiation of an oxygen-free MeCN solution of **1a**—**e** (5.0—50×10^{-4} M, 1 M = 1 mol dm^{-3}) containing BP (3.0×10^{-2} M) with 366 nm light resulted in the appearance of the corresponding *p*-substituted *N*-(*p*-substituted benzylidene)benzylamine derivatives **2a**—**e** and 1-naphthoic acid (**3**) in addition to a negligible amount of naphthalene (Scheme 1). The quantum yields (Φ) for the appearance of the products were determined by using a potassium tris(oxalato)ferrate(III) actinometer,[8] whereas we could not estimate accurately the Φ value for the disappearance of the starting **1** owing to the appreciably low reaction efficiency (Φ = 0.02—0.03). It was previously shown that the decarboxylation product, anisole, is derived from the *p*-anisoyloxyl radical that escaped from the initially-formed triplet cage in competition with its highly efficient spin inversion to the singlet cage where hydrogen abstraction (giving the elimination products) and recombination (affording the starting material) occur exclusively.[5] Accordingly, the negligible formation of naphthalene leads us to propose Scheme 2, which allows us to derive Eq. 1 under the steady-state approximation,

$$1/\Phi_2 = 1/\Phi_3 = (1+k_d/k_r)(1+1/k_t\tau_T[\mathbf{1}]), \tag{1}$$

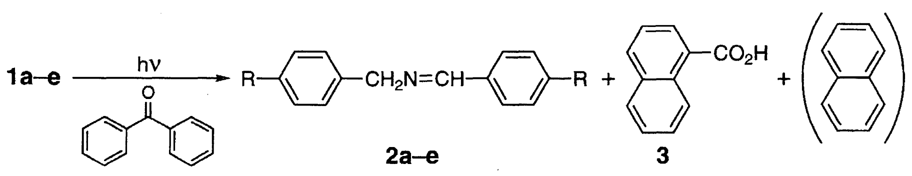
where Φ_2 and Φ_3 are the quantum yields for appearance of the imine **2** and 1-naphthoic acid (**3**), respectively. An inspection of Eq. 1 indicates that the reciprocal of Φ ($1/\Phi$) varies linearly with the reciprocal of the starting hydroxylamine concentration ($1/[\mathbf{1}]$), while the slope of the linear plot is expected to become very small because of the extremely large quenching constant, $k_t\tau_T$. In fact, the typical double reciprocal plots shown in Fig. 2 demonstrate that the quantum



Scheme 2.

Table 1. Quenching Constants and Energy-Transfer Rate Constants for the **1**–BP System and Excitation Energies of **1a**—**e**

Compound	$k_t\tau_T/10^5$ M^{-1}	$k_t/10^{10}$ M^{-1} s^{-1}	E_S/kJ mol^{-1}	E_T/kJ mol^{-1}
1a	4.2	1.6	370	247
1b	7.1	2.7	370	246
1c	5.5	2.1	370	247
1d	5.5	2.1	370	246
1e	5.9	2.3	370	246



Scheme 1.

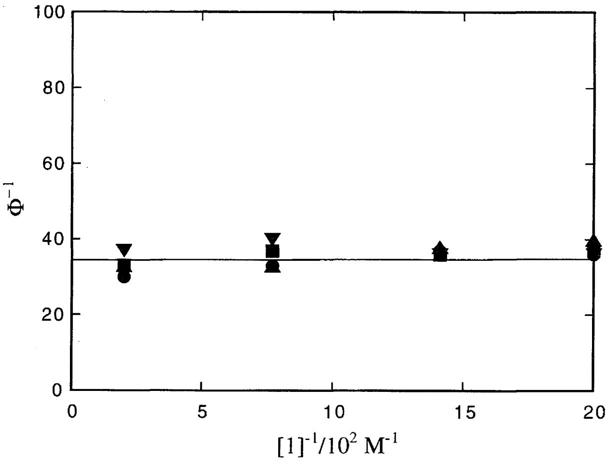


Fig. 2. Stern-Volmer plots of Φ_{2b}^{-1} (●), Φ_3^{-1} (▲), Φ_{2e}^{-1} (■), and Φ_3^{-1} (▼) versus $[\mathbf{1}]^{-1}$ for the BP (0.030 M)-sensitized photolyses of **1b** (●,▲) and **1e** (■,▼) with 366 nm light in O_2-free MeCN at room temperature.

yields for the reaction are apparently independent of [**1**]. For this reason, the limiting quantum yields (Φ_{lim}) were obtained by taking an average of the Φ value determined at each **1a**—**e** concentration, and are collected in Table 2 along with the k_r/k_d values that were evaluated based on the relation $1/\Phi_{2,\text{lim}} = 1+k_d/k_r$.

Discussion

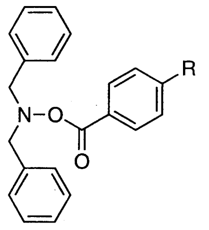
In a previous study,[5] we showed that triplet-triplet energy transfer between BP ($E_T = 290$ kJ mol^{-1}) and *O*-(*p*-substituted benzoyl)-*N*,*N*-dibenzylhydroxylamines (**4**; E_T = 280—289 kJ mol^{-1}) proceeds at the rate (k_t = 1.8—2.4$\times10^6$ M^{-1} s^{-1}), which is much smaller than the diffusion-controlled rate ($k_{\text{DIF}} = 2.9\times10^{10}$ M^{-1} s^{-1} in MeCN at 25 °C). Because both molecules have almost the same triplet energies, reversible energy transfer may be responsible for the slow transfer rate observed for **4**. On the other hand, the large exothermicity for energy-transfer process between triplet BP and **1** (ΔE_T = 76—80 kJ mol^{-1}) renders this process energetically very favorable, and is consistent with the fact that exothermic triplet–triplet energy transfer proceeds at the diffusional rate and is insensitive to an electronic configurational change which occurs during this energy transfer.[9] This highly efficient energy transfer allows us to predict the occurrence of a N–O bond cleavage for triplet **1** in large quantum yield. An inspection of the limiting quantum yields for the appearance of the imine **2** and the carboxylic acid **3** demonstrates, however, that the imine-forming radical elimination takes place only at a low quantum efficiency of 2—3%. The previous finding,[5] that the *O*-*p*-substituted benzoyl system **4a**—**c** (Chart 2) in the triplet excited state gives radical elimination products in 10—20% limiting quantum yields, suggests that in addition to the recombination efficiency of the aminyl and aroyloxyl radicals in the singlet cage, the electronic configuration (n,π* or π,π*) of the triplet **1** and **4** is also a factor in determining the net N–O bond-cleavage efficiency.

Table 2. Limiting Quantum Yields and k_r/k_d Values for the BP-Sensitized Photolysis of **1a**—**e** in N_2-Purged MeCN at Room Temperature

Compound	$\Phi_{2,\text{lim}}$	$\Phi_{3,\text{lim}}$	k_r/k_d
1a	0.025	0.029	0.026
1b	0.030	0.028	0.031
1c	0.026	0.026	0.027
1d	0.025	0.025	0.026
1e	0.028	0.027	0.029

As already described, the elimination products are obtained solely by hydrogen abstraction of the aroyloxyl radical from the aminyl within the singlet cage, and this abstraction takes place in competition with the recombination of these two radicals that affords the starting hydroxylamine. Since *p*-substituted benzoyloxyl radicals possess reactivities that are not very different from those of the 1-naphthoyloxyl radical,[10] it is much less likely that the abilities of these aroyloxyl radicals to abstract hydrogen and to recombine in the cage become major factors controlling the magnitude of the limiting quantum yields for the reaction.

It is well-known that phosphorescence emitted from the n,π* triplet excited state has a much shorter lifetime (τ_T) than that of emission from the π,π* state.[9] A comparison between the phosphorescence lifetimes of 2-acetylnaphthalene (τ_T = 300 μs)[6] and acetophenone (τ_T = 0.2 μs)[6] indicates that a replacement of the naphthyl group by phenyl enhances the n,π* nature in the triplet excited state. The difference in the electronic configuration between the lowest triplet excited states of model compounds **1** and **4** is also considered to be reflected in the vibrational progression of their phosphorescence spectra.[9] Figure 3 shows that energy spacing between the vibrational structures of the former spectrum is in the range of about 1400 to 1500 cm^{-1}, whereas there is no clear progression in the latter spectrum. Because the spacing of 1400—1500 cm^{-1} is attributable to the C=C stretching vibration of the naphthalene ring, we are led to conclude that model **1b** possesses a triplet excited state of a strong π,π* character. Thus, it is very likely that the triplet excitation energy transferred from BP to **1** is largely localized on the naphthalene ring, and thus cannot be effectively utilized for N–O bond fission. If one assumes triplet **4** with an n,π* configuration, it is expected that the excitation energy could migrate to the carbonyl group, resulting in a more ef-



4a–c

R= OMe (**4a**), F (**4b**), CF_3 (**4c**)

Chart 2.

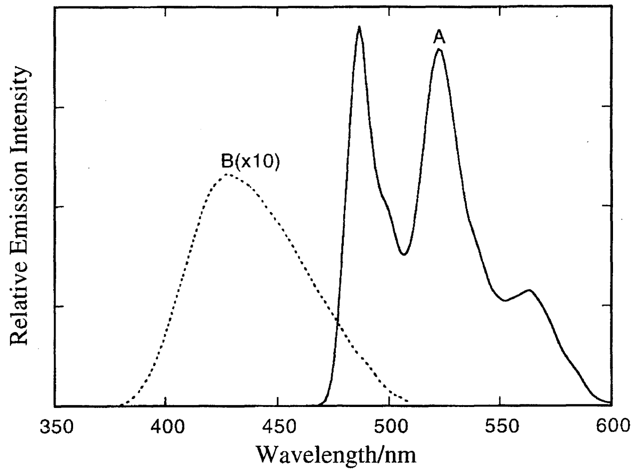


Fig. 3. Phosphorescence spectra of **1b** (A; 1.0×10^{-3} M) and **4a** (B; 1.0×10^{-3} M) in butyronitrile at 77 K. Excitation wavelength is 300 nm.

ficient cleavage of the N–O bond in triplet **4** than in triplet **1**. Although the weak phosphorescence of **4a** provided no information regarding the electronic configuration of this molecule, the finding that the limiting quantum yields for a sensitized reaction of **4** are about 5- to 7-times those for the reaction of **1**, therefore, strongly suggests that the triplet excited state of **4** must have an n,π* nature, at least, to some extent.

A Hammett analysis of the correlation of rates with substituent constants provides significant information about the transition-state structure for both heterolytic and homolytic cleavages of a specific bond. It was previously shown that the triplet-state deactivation (k_d) of the model hydroxylamine **4** should undergo a much less-sensitive electronic effect of the substituent than does the N–O bond cleavage process (k_r), thus allowing us to use the $k_\mathrm{r}/k_\mathrm{d}$ value for the Hammett analysis.[5a] In addition, the logarithm of the $k_\mathrm{r}/k_\mathrm{d}$ exhibited a Hammett-type linear relationship with a slope (ρ) of -0.75. This finding led us to propose the transition-state structure (for homolytic N–O bond cleavage in the triplet excited state) to which the ionic structure contributes to a relatively large extent. As demonstrated in Fig. 4, the magnitude of $\log(k_\mathrm{r}/k_\mathrm{d})$ shows a negligible dependence on the substituent constant, σ. On the other hand, the Hammett analysis of substituent effects on the proton dissociation reactions of benzoic acid ($\rho = 1.00$) and phenylacetic acid ($\rho = 0.56$) confirmed that the introduction of a methylene spacer chain lowers the ρ value by nearly half.[11] Taking into consideration that the presence of a substituent on each benzene ring in the model hydroxylamine **1** used in this study should compensate for this decrease in ability to transmit an electronic effect to a certain extent, we are able to conclude that the N–O bond of **1** in the triplet excited state is cleft via the transition state **I** (Chart 3) with, if any, a very small ionic character. The difference in the transition-state structure for the N–O bond cleavage process between **1** and **4** may be related to the electronic configuration in the lowest triplet excited states of these two model hydroxylamines.

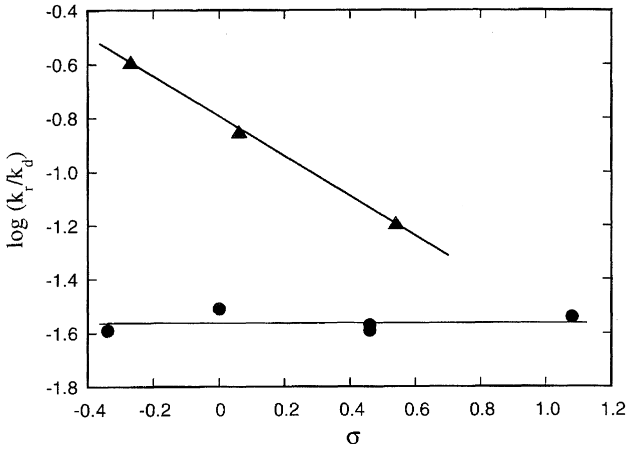
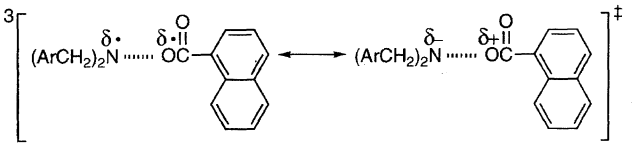


Fig. 4. Correlation of $\log(k_\mathrm{r}/k_\mathrm{d})$ with σ values for the BP-sensitized photolyses of **1** (●) and **4** (▲) with 366 nm light in MeCN.



I

Chart 3.

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 (220 and 240 nm). IR spectra were taken with a Hitachi Model 270-30 infrared spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL Model JNM-500 spectrometer. In addition to fluorescence of the starting hydroxylamines, room-temperature phosphorescences of benzophenone with and without these hydroxylamines were 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-2200 spectrophotometer and a Hitachi Model F-4500 spectrofluorimeter equipped with attachments for measuring low-temperature phosphorescence, respectively.

Materials and Solvents. *N*,*N*-Bis(*p*-substituted benzyl)hydroxylamines were prepared from the reactions of *p*-substituted benzyl chlorides with hydroxylamine in a refluxing aqueous ethanol solution, according to the method of Jones and Sneed.[12] *O*-Acylation of these hydroxylamines with 1-naphthoyl chloride in dichloromethane containing equimolecular amounts of pyridine gave *O*-(1-naphthoyl)-*N*,*N*-bis(*p*-substituted benzyl)hydroxylamines in good yields. The crude products were purified by column chromatography over silica gel (70—230 mesh, Merck) using chloroform as an eluent, followed by recrystallization from ethyl acetate–hexane to afford colorless crystals with the following physical and spectroscopic properties.

***O*-(1-Naphthoyl)-*N*,*N*-bis(*p*-methylbenzyl)hydroxylamine (1a).** Mp 99.5—100.5 °C; IR (KBr) 1760 and 1245 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 2.32$ (6H, s), 4.21 (4H, s), 7.13 (4H, d, $J = 7.9$ Hz), 7.34 (1H, dd, $J = 7.3$, 8.2 Hz), 7.38 (4H, d, $J = 7.9$ Hz), 7.40 (1H, ddd, $J = 1.2$, 6.7, 7.9 Hz), 7.45 (1H, ddd, $J = 1.2$, 6.7, 7.9 Hz), 7.56 (1H, dd, $J = 1.2$, 7.3 Hz), 7.79 (1H, dd,

$J = 1.2$, 8.2 Hz), 7.89 (1H, d, $J = 8.2$ Hz), and 8.09 (1H, d, $J = 8.5$ Hz); ^{13}C NMR (CDCl$_3$) $\delta = 21.16$, 62.28, 124.35, 125.69, 126.17, 127.28, 127.54, 128.20, 128.40, 129.07, 129.45, 130.80, 132.36, 133.15, 133.54, 137.29, and 166.21. Found: C, 82.04; H, 6.32; N, 3.34%. Calcd for C$_{27}$H$_{25}$NO$_2$: C, 82.00; H, 6.37; N, 3.54%.

***O*-(1-Naphthoyl)-*N*,*N*-dibenzylhydroxylamine (1b).** Mp 57.5—58.5 °C; IR (KBr) 1750 and 1240 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 4.27$ (4H, s), 7.26—7.30 (2H, m), 7.32—7.35 (5H, m), 7.41 (1H, ddd, $J = 1.5$, 6.7, 8.3 Hz), 7.45 (1H, ddd, $J = 1.5$, 6.7, 8.2 Hz), 7.50—7.53 (5H, m), 7.79 (1H, dd, $J = 1.5$, 8.5 Hz), 7.89 (1H, d, $J = 8.2$ Hz), and 8.09 (1H, dd, $J = 1.2$, 8.5 Hz); ^{13}C NMR (CDCl$_3$) $\delta = 62.66$, 124.34, 125.56, 126.19, 127.40, 127.71, 128.21, 128.39, 128.42, 129.43, 130.77, 132.42, 133.53, 136.20, and 166.19. Found: C, 81.61; H, 5.79; N, 3.69%. Calcd for C$_{25}$H$_{21}$NO$_2$: C, 81.72; H, 5.76; N, 3.81%.

***O*-(1-Naphthoyl)-*N*,*N*-bis(*p*-chlorobenzyl)hydroxylamine (1c).** Mp 121.0—122.0 °C; IR (KBr) 1770 and 1240 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 4.20$ (4H, s), 7.31 (4H, d, $J = 8.5$ Hz), 7.36 (1H, dd, $J = 7.3$, 8.2 Hz), 7.44 (4H, d, $J = 8.2$ Hz), 7.45—7.49 (2H, m), 7.53 (1H, dd, $J = 1.2$, 7.3 Hz), 7.79—7.82 (1H, m), 7.92 (1H, d, $J = 8.2$ Hz), and 8.04—8.06 (1H, m); ^{13}C NMR (CDCl$_3$) $\delta = 62.00$, 124.32, 125.34, 126.37, 126.93, 127.57, 128.30, 128.33, 128.66, 130.71, 130.74, 132.71, 133.58, 133.73, 134.50, and 165.98. Found: C, 68.53; H, 4.61; N, 3.06%. Calcd for C$_{25}$H$_{19}$Cl$_2$NO$_2$: C, 68.82; H, 4.39; N, 3.21%.

***O*-(1-Naphthoyl)-*N*,*N*-bis(*p*-bromobenzyl)hydroxylamine (1d).** Mp 139.5—140.5 °C; IR (KBr) 1760 and 1240 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 4.19$ (4H, s), 7.36 (1H, dd, $J = 7.0$, 8.2 Hz), 7.38 (4H, d, $J = 8.5$ Hz), 7.46 (4H, d, $J = 8.2$ Hz), 7.45—7.49 (2H, m), 7.52 (1H, dd, $J = 1.2$, 7.0 Hz), 7.80—7.82 (1H, m), 7.93 (1H, d, $J = 8.2$ Hz), and 8.02—8.05 (1H, m); ^{13}C NMR (CDCl$_3$) $\delta = 62.06$, 121.88, 124.32, 125.33, 126.38, 126.92, 127.61, 128.29, 128.33, 130.74, 131.06, 131.63, 132.72, 133.58, 134.99, and 165.96. Found: C, 57.29; H, 3.79; N, 2.41%. Calcd for C$_{25}$H$_{19}$Br$_2$NO$_2$: C, 57.17; H, 3.65; N, 2.67%.

***O*-(1-Naphthoyl)-*N*,*N*-bis[*p*-(trifluoromethyl)benzyl]hydroxylamine (1e).** Mp 157.5—158.5 °C; IR (KBr) 1770 and 1245 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 4.32$ (4H, s), 7.34 (1H, dd, $J = 7.0$, 8.2 Hz), 7.42 (1H, ddd, $J = 1.2$, 6.7, 8.6 Hz), 7.47 (1H, ddd, $J = 1.2$, 7.4, 7.4 Hz), 7.47 (1H, dd, $J = 1.2$, 7.4 Hz), 7.61 (4H, d, $J = 8.0$ Hz), 7.66 (4H, d, $J = 7.9$ Hz), 7.80 (1H, d, $J = 7.4$ Hz), 7.92 (1H, d, $J = 8.6$ Hz), and 8.00 (1H, d, $J = 8.6$ Hz); ^{13}C NMR (CDCl$_3$) $\delta = 62.40$, 124.13 (q, $J = 272$ Hz), 124.28, 125.14, 125..49 (q, $J = 4$ Hz), 126.45, 126.63, 127.65, 128.30, 128.39, 129.61, 130.26 (q, $J = 32$ Hz), 130.75, 132.91, 133.61, 139.96, and 165.89. Found: C, 64.61; H, 4.00; N, 2.47%. Calcd for C$_{27}$H$_{19}$F$_6$NO$_2$: C, 64.41; H, 3.80; N, 2.78%.

N-Benzylidenebenzylamine (**2b**) was commercially available and purified by fractional distillation under reduced pressure. Previously prepared and purified *p*-bromo-*N*-(*p*-bromobenzylidene)benzylamine (**2d**) and *O*-(*p*-anisoyl)-*N*,*N*-dibenzylhydroxylamine (**4a**) were used without further purification.[5b] The condensation reactions between *p*-substituted benzylamines and *p*-substituted benzaldehydes in refluxing dry benzene afforded *p*-substituted *N*-(*p*-substituted benzylidene)benzylamines, which were recrystallized from dry hexane–benzene to give analytically pure authentic samples **2a**, **2c**, and **2e** with the following physical and spectroscopic properties:

***p*-Methyl-*N*-(*p*-methylbenzylidene)benzylamine (2a).** Mp 83.5—84.5 °C; IR (KBr) 1640 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 2.33$ (3H, s), 2.38 (3H, s), 4.76 (2H, s), 7.14 (2H, d, $J = 7.9$ Hz), 7.20—7.22 (4H, m), 7.66 (2H, d, $J = 7.9$ Hz), and 8.33 (1H, s); ^{13}C NMR (CDCl$_3$) $\delta = 21.09$, 21.49, 64.80, 127.96, 128.25, 129.15, 129.29, 133.68, 136.40, 136.50, 140.95, and 161.65. Found: C, 85.95; H, 7.54; N, 6.03%. Calcd for C$_{16}$H$_{17}$N: C, 86.05; H, 7.67; N, 6.27%.

***p*-Chloro-*N*-(*p*-chlorobenzylidene)benzylamine (2c).** Mp 65.5—66.5 °C; IR (KBr) 1640 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 4.77$ (2H, s), 7.27 (2H, d, $J = 8.2$ Hz), 7.31 (2H, d, $J = 8.2$ Hz), 7.39 (2H, d, $J = 8.2$ Hz), 7.71 (2H, d, $J = 8.2$ Hz), and 8.34 (1H, s); ^{13}C NMR (CDCl$_3$) $\delta = 64.19$, 128.67, 128.95, 129.27, 129.47, 132.87, 134.51, 136.92, 137.63, and 160.83. Found: C, 63.67; H, 4.42; N, 4.96%. Calcd for C$_{14}$H$_{11}$Cl$_2$N: C, 63.66; H, 4.20; N, 5.30%.

***p*-Trifluoromethyl-*N*-[*p*-(trifluoromethyl)benzylidene]benzylamine (2e).** Mp 36.0—37.0 °C; IR (KBr) 1650 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) $\delta = 4.90$ (2H, s), 7.47 (2H, d, $J = 7.9$ Hz), 7.62 (2H, d, $J = 7.9$ Hz), 7.69 (2H, d, $J = 7.9$ Hz), 7.91 (2H, d, $J = 7.9$ Hz), and 8.46 (1H, s); ^{13}C NMR (CDCl$_3$) $\delta = 64.42$, 123.90 (q, $J = 272$ Hz), 124.23 (q, $J = 272$ Hz), 125.51 (q, $J = 4$ Hz), 125.67 (q, $J = 4$ Hz), 128.14, 128.54, 129.50 (q, $J = 32$ Hz), 132.63 (q, $J = 32$ Hz), 139.01, 143.01, and 161.10. Found: C, 58.25; H, 3.52; N, 4.04%. Calcd for C$_{16}$H$_{11}$F$_6$N: C, 58.01; H, 3.35; N, 4.23%.

Benzophenone and 1-naphthoic acid were purified by repeated recrystallization from ethanol and aqueous ethanol, respectively. Naphthalene was of scintillation grade and was used as received. Purification of acetonitrile and butyronitrile were accomplished by the standard methods.[13]

Quantum Yields. A potassium tris(oxalato)ferrate(III) actinometer was employed to determine the quantum yields for the benzophenone-sensitized imine-forming radical elimination at low conversions (<3%) of the starting **1a**—**e**.[8] 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 7-60, and Toshiba IRA-25S glass filters. Linear calibration curves for each product, made under the same analytical conditions, were utilized to quantify the appearance of **2a**—**e** and **3**. All of the quantum yields are an average of more than seven determinations.

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