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The Mechanisms of Photochemical Reactions of *o*-Sulfobenzoic Imides

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The photochemical processes of *N*-propyl-*o*-sulfobenzoic imide to the amides were investigated in ethanol and monocyclic aromatics, such as benzene, anisole, toluene, polymethylbenzenes, and benzonitrile. It was clarified that although both the S_1 and T_1 states took part in those photochemical reactions, the mechanisms were different in ethanol and those aromatics. The mechanism in ethanol is thought to involve hydrogen-atom abstraction from ethanol by a diradical formed after the extrusion of sulfur dioxide. The mechanism in aromatics involved an energy transfer from the singlet excited aromatic molecules to the sulfobenzoic imide and the addition of the resulting diradicals to the partner aromatics. Although the sulfobenzoic imide sensitized to a triplet state by acetophenone in benzene resulted as well in the formation of the arylated benzamide, this process was minor in comparison with the process via the S_1 state. This was attributed to the triplet multiplicity of the diradical. The reactions of the sulfobenzoic imide with *p*-xylene and mesitylene were less predominant than those with toluene and anisole, which was attributable to a steric effect of plural methyl groups on the ring. The fact that no formation of the arylated benzamides took place in the case of benzonitrile could be explained by a strong inductitive effect of a cyano group of benzonitrile.

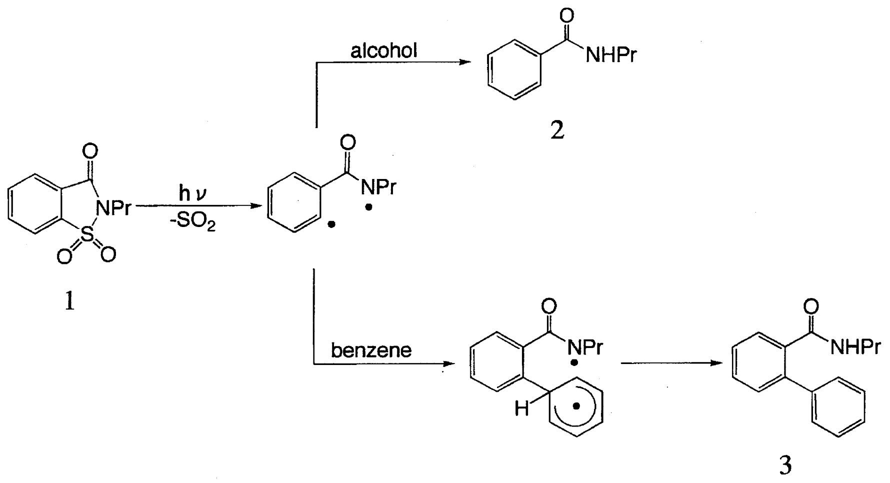
Various types of reactions developed after the extrusion of sulfur dioxide from cyclic sulfonyl compounds, and their related derivatives are still attractive to us from the view point of physical chemistry and chemical synthesis.[1—3] The photochemical extrusion of sulfur dioxide from cyclic sulfonamides forms a diradical to cause cyclization.[4] Kamigata et al. reported that the irradiation of *N*-alkyl-*o*-sulfobenzoic imides, for example *N*-propyl-*o*-sulfobenzoic imide (**1**), resulted in the formation of *N*-propylbenzamide (**2**) in 2-propanol and *N*-propyl-*o*-phenylbenzamide (**3**) in benzene (Scheme 1).[5] They suggested that both reactions proceeded through a diradical intermediate formed after the extrusion of sulfur dioxide. The former process is hydrogen-atom abstraction from 2-propanol by the diradical, and the latter is intramolecular hydrogen-atom abstraction in a cyclohexadienyl radical formed by benzene addition to the diradical. Although there has been no further report concerning the photolysis of sulfobenzoic imides to the best of our knowledge, a similar situation has been observed in the photolysis and/or thermolysis of benzotriazoles and their derivatives. The irradiation of benzotriazoles eliminates a nitrogen molecule to form iminocyclohexadienylidene, which undergoes the well-known Wolff rearrangement and cyclization to form carbazoles[6,7] as well as reactions[8,9] similar to those of diradicals generated from sulfobenzoic imides. Studies by ESR concerning the photolysis of benzotriazole and its derivatives at 77 K demonstrated that the observed diradicals were in the triplet state.[10] However, Shizuka et al. reported that diradicals originating from benzotriazole rapidly reached thermal equilibrium between the singlet and triplet manifolds over 77 K, and showed different reactivities in both states.[11] Our interest in *o*-sulfobenzoic imides is directed to the multiplicities of the electronic excited states and the diradical intermediates involved in the photochemical reactions. Most of the 254-nm light irradiated to the benzene solutions of *o*-sulfobenzoic imides must be absorbed by benzene, and the reaction may involve energy transfer from excited benzene to the imides in a mechanism which is expected to be different from that in alcoholic solvents.

In the present studies, the quantum yields of the photochemical reactions of **1** in ethanol and benzene were measured, and the photochemical reactions of **1** with several monocyclic aromatics were tried as well.

Results and Discussion

A preliminary irradiation of **1** with a low-pressure mercury lamp under a nitrogen atmosphere gave **2** and **3** reported by Kamigata et al., in yields of 32 and 63% in ethanol and benzene, respectively.

Quantum Yields Determination. The triplet excitation energy (E_T) of **1** was determined to be about 296 kJ mol^{-1} from the first maximum of the phosphorescence spectra in an EPA solution at 77 K. The estimated lifetime of 2.3 ms indicates that the triplet state of **1** is of $n\pi^*$ character. 2,3-Butanedione ($E_T = 235$ kJ mol^{-1}) may be used as a preferred triplet quencher in the photochemical reaction of **1**, because its molar absorption coefficient ($\varepsilon = 14$ M^{-1} cm^{-1} at 254 nm, M = mol dm^{-3}) is quite small in comparison with those of dienes, such as isoprene ($\varepsilon = 40$ M^{-1} cm^{-1} at 254 nm) and 1,3-pentadienes ($\varepsilon = 20$ and 50 M^{-1} cm^{-1} for *cis*- and *trans*-, respectively).[12] A triplet quenching effect on the quantum yields was measured in ethanol and benzene solutions at a



Scheme 1.

concentration of 5×10^{-4} mol dm^{-3} of **1**. The molar-absorption coefficient of **1** at 254 nm was 1900 M^{-1} cm^{-1} in ethanol. Therefore, the absorption of 254-nm light by 2,3-butanedione could be neglected under these conditions.

Upon the 254-nm light irradiation of an ethanol solution of **1** the quantum yield in the formation of **2** was 0.030 in the absence of a quencher. A Stern–Volmer plot is shown in Fig. 1. Saturation of the plot in a higher region of a quencher concentration indicated that both the S_1 and T_1 states were closely related to the formation of **2**. It is reasonably concluded that the extrusion of sulfur dioxide occurs in both S_1 and T_1 states to form a diradical which brings about hydrogen-atom abstraction from ethanol. From the Stern–Volmer plot, the ratio of the T_1 state responsible for this reaction was estimated to be four sevenths.

The quantum yield in the formation of **2** was only 0.0045 in tetrahydrofuran. Similar irradiation in less hydrogen-donating solvents, cyclohexane and acetonitrile, hardly caused any photochemical change. The photochemical extrusion of sulfur dioxide from **1** is characterized by depending on the hydrogen-donating ability of solvents in contrast to the case of benzotriazoles, which form diradicals even in acetonitrile.[13]

Figure 2a shows the quantum yield in the formation of **3** by the 254-nm light irradiation of a benzene solution of **1** (5×10^{-4} mol dm^{-3}) in the presence of 2,3-butanedione. The values were independent on the quencher concentration, indicating that the formation of **3** took place exclusively from the S_1 state. The molar-absorption coefficients of benzene

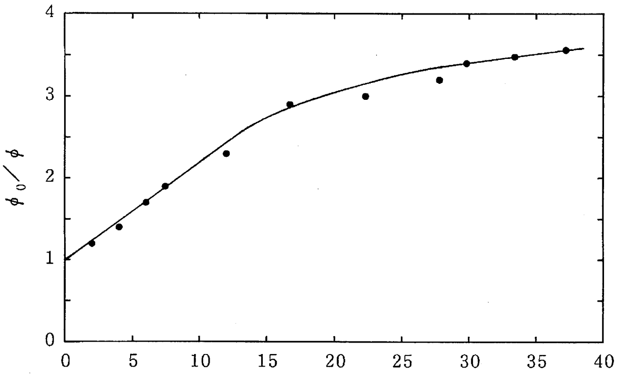


Fig. 1. Stern–Volmer plot of the quantum yields of **2** for the triplet quencher on irradiation in ethanol.

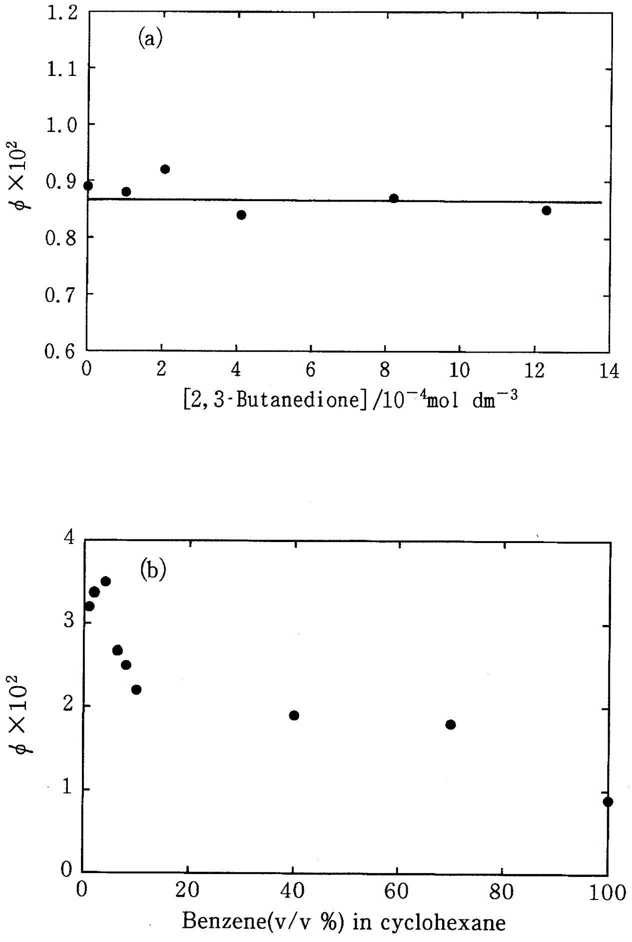


Fig. 2. (a) Effect of the triplet quencher on the quantum yields of **3** on irradiation in benzene. (b) Change of the quantum yields of **3** against the concentration of benzene in cyclohexane.

and **1** are 90 and 1900 $M^{-1}\,cm^{-1}$ at 254 nm, respectively. Then, under the present experimental conditions, where the concentration of **1** was 5×10^{-4} mol dm^{-3}, the estimated amount of light absorbed by **1** was only one thousandth of the incident light. The quantum yield in the formation of **3** in benzene was 0.0089, which was too high, provided that the diradical formed from the directly excited **1** reacted with benzene to form **3**. The S_1 state energy level of benzene is 468 kJ mol^{-1}[12] and that of **1** was roughly estimated at 417 kJ mol^{-1} on the basis of the longest wavelength of its absorption spectrum, because no clear fluorescence of **1** was observed. Thus, it reasonably follows that an initially excited species is a benzene molecule and the path to **3** involves an energy transfer from a singlet excited benzene molecule to **1**. As shown in Table 1, the quantum yield in the formation of **3** increased as the solute concentration increased. Such a concentration effect supports our idea that this reaction proceeds via a collision of excited benzene with **1**. According to Cundall et al.,[14] singlet excited benzene goes to a triplet state through a singlet excimer with a quite high intersystem crossing efficiency, wherein it is found that the quantum yield of intersystem crossing decreases to 0.23 in a 1%-benzene solution diluted by cyclohexane (v/v) from 0.56 in pure benzene. Figure 2b shows that the quantum yield of **3** is considerably dependent on the concentration of benzene in cyclohexane. The rise in Φ over 0.03 in a much lower concentration region may be ascribed to a decreased self-quenching process of singlet excited benzene to a triplet state. Absorption by **1** reaches about 10% of the incident light in a 1%-benzene solution, and the reaction from directly excited **1** is considered to contribute to a small increase of Φ. Product **2** was not found even in diluted benzene–cyclohexane solutions. The substantial absence of **2** demonstrates that the addition of the resulting diradical to the partner benzene precedes exclusively hydrogen-atom abstraction from cyclohexane.

The photochemical reaction of **1** in ethanol occurred in the T_1 state as well as the S_1 state. As described above, the quantum yield in the formation of triplet benzene is 0.56, and, accordingly, it seems reasonable to consider that triplet benzene or triplet **1** might be involved in the formation of **3**. However, Fig. 2a shows no triplet quenching effect on the yield of **3**, indicating that the path to **3** via the T_1 state is trivial. The energy levels of triplet benzene and its excimer are 352[12] and 299 kJ mol^{-1},[15] respectively, and both states can be adequately quenched by 1,3-butanedione. Probably, the addition of the triplet diradical to benzene is considered to be inefficient. Consequently, the main photochemical process of **1** in a benzene solution can be expressed by the following scheme:

$$\mathrm{B} \xrightarrow{254\ \mathrm{nm}} {}^1\mathrm{B}^* \tag{1}$$

$${}^1\mathrm{B}^* + \mathbf{1} \longrightarrow \mathrm{B} + \mathbf{1}^* \xrightarrow[-\mathrm{SO_2}]{} \mathrm{B}\cdots\mathrm{Diradical} \longrightarrow \mathbf{3} \tag{2}$$

$${}^1\mathrm{B}^* + \mathrm{B} \longrightarrow {}^1\mathrm{B}_2 \longrightarrow {}^3\mathrm{B}_2 \tag{3}$$

$${}^1\mathrm{B}^* \longrightarrow {}^3\mathrm{B}^* \tag{4}$$

$${}^3\mathrm{B}^* + \mathbf{1} \longrightarrow \mathbf{3} \tag{5}$$

B: Benzene

Table 1. Effect of Concentration of **1** on the Quantum Yields of the Formation of **3**

$\dfrac{[\mathbf{1}]\times10^4}{\mathrm{mol\,dm^{-3}}}$	Φ
2.08	0.0073
4.97	0.0089
8.79	0.012
18.32	0.015
26.92	0.016

Triplet Sensitization by Acetophenone. In order to examine the participation of the T_1 state in the formation of **3**, triplet sensitization by acetophenone (E_T=308 kJ mol^{-1}) was tried. A benzene solution containing acetophenone (0.2 mol dm^{-3}) and **1** (4×10^{-3} mol dm^{-3}) was irradiated under a nitrogen atmosphere by 366-nm light from a high-pressure mercury lamp, wherein acetophenone was only excited. By analogy with nitrenes,[16] the triplet-sensitized **1** may provide a triplet diradical after the extrusion of sulfur dioxide. The observed quantum yield ($\Phi_{T(obs)}$) in the formation of **3** was only 0.0007. The photochemical process of **1** by acetophenone sensitization can be shown in the following process, wherein Φ_T is the quantum yield in the formation of **3** from the triplet **1**:

$$\mathrm{Acp} \xrightarrow{366\ \mathrm{nm}} {}^1\mathrm{Acp}^* \tag{6}$$

$${}^1\mathrm{Acp}^* \xrightarrow{\Phi_{\mathrm{ISC}}} {}^3\mathrm{Acp}^* \tag{7}$$

$${}^3\mathrm{Acp}^* + \mathbf{1} \xrightarrow{k_d} \mathrm{Acp} + {}^3\mathbf{1}^* \tag{8}$$

$${}^3\mathrm{Acp}^* \xrightarrow{k_r} \mathrm{Acp} \tag{9}$$

$${}^3\mathbf{1}^* \xrightarrow[-\mathrm{SO_2}]{k_f} {}^3\mathrm{Diradical} \tag{10}$$

$${}^3\mathrm{Diradical} + \mathrm{B} \longrightarrow \mathbf{3} \tag{11}$$

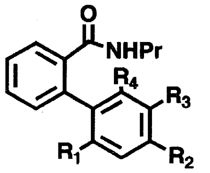
Acp: Acetophenone

Then, $\Phi_{T(obs)}$ can be shown by the following equation:

$$\Phi_{\mathrm{T(obs)}} = \Phi_{\mathrm{ISC}} \frac{k_d\,[\mathbf{1}]}{k_r + k_d\,[\mathbf{1}]} \times \Phi_{\mathrm{T}}. \tag{12}$$

The efficiency of the intersystem crossing (Φ_{ISC}) of acetophenone is estimated to be 1.0 and its triplet lifetime (τ) is 3.5 μs in benzene, indicating that the radiationless rate constant to the ground state ($k_r(1/\tau)$) is 2.9×10^5 s^{-1}.[12] The rate of energy transfer from triplet acetophenone to **1** can be replaced by the rate of diffusion in benzene ($k_d=1.0\times10^{10}$ dm^3 mol^{-1} s^{-1} at 20 °C). Therefore, under this experimental condition that the concentration of **1** is 4.0×10^{-3} mol dm^{-3}, most of the triplet acetophenone molecules may encounter **1** to form the triplet **1**. Therefore, it is possible to neglect k_r in comparison with k_d [**1**] in Eq. 12. Conclusively, Φ_T is nearly equal to $\Phi_{T(obs)}$, the value of which is much lower than the

Table 2. Yields of the Photoproducts in Several Monocyclic Aromatics by 8 h Irradiation



3 : R_1=R_2=R_3=R_4=H
4a : R_1=Me, R_2=R_3=R_4=H
4b : R_1=R_3=R_4=H, R_2=Me
5a : R_1=OMe, R_2=R_3=R_4=H
5b : R_1=R_3=R_4=H, R_2=OMe
6 : R_1=R_3=Me, R_2=R_4=H
7 : R_1=R_2=R_4=Me, R_3=H

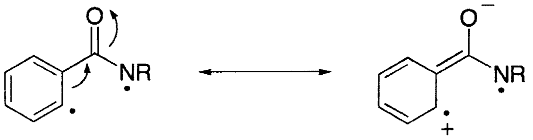
Solvent	(E_s/kJ mol^{-1})[12]	Conversion/%	Yield/(%)
Benzene	(468)	60	**3** (63)
Toluene	(443)	65	**4a** (30), **4b** (21)
Anisole[a]	(431)	76	**2** (5), **5a** (41), **5b** (15)
p-Xylene[b]	(435)	93	**2** (19), **6** (41)
Mesitylene[c]	(439)	29	**2** (46), **7**(trace)
Benzonitrile[d]	(435)	33	**2** (55)

a) [Anisole]=5×10^{-2} M in THF, b) [*p*-Xylene]=1.4×10^{-1} M in THF, c) [Mesitylene]=2.2×10^{-1} M in THF, d) [Benzonitrile]=3.2×10^{-1} M in THF.

value in the S_1 state of **1**. When **1** was sensitized by acetophenone, many by-products were formed, and the chemical yield of **3** was only 10%. Therefore, such a lower yield of **3** from triplet **1** can be attributed to the uneffectiveness of the triplet diradical in arylation.

The addition of benzene to diradicals produced from benzotriazoles is suggested to occur in a singlet excited state, but not a triplet state. The difference in the behavior between the singlet and triplet diradicals has been explained by a difference in the electronic structure. Platz et al. reported that the photolysis of pentafluorophenyl azide in toluene resulted in the formation of the ortho and para adducts from the singlet nitrene and benzylic insertion adduct from the triplet nitrene.[17] As described later, the 254-nm irradiation of a toluene solution containing **1** gave the corresponding *ortho*- and *para*-substituted adducts, but not the benzylic insertion adduct. By analogy with those results, the formation of **3** via the triplet diradical (Eq. 11) may be attributed to the singlet diradical formed through intersystem crossing, which competes with more predominant decomposing processes.

Photochemical Reaction of 1 with Monocyclic Aromatic Molecules. The photochemical reactions of **1** with toluene, anisole, *p*-xylene, mesitylene, and benzonitrile were carried out under similar conditions with preliminary irradiation in ethanol or benzene. Those aromatics have higher S_1 state-energy levels than that of **1**. Those aromatics, except for toluene, were diluted by tetrahydrofuran to such an extent that the 254-nm incident light absorbed by those aromatics was about 75%, because removing those from the reaction solution was difficult. Table 2 shows the yields of the products. The photochemical reactions of **1** with toluene and anisole gave two types of arylated benzamides, respectively: 2-(2-methylphenyl)-*N*-propylbenzamide (**4a**) and 2-(4-methylphenyl)-*N*-propylbenzamide (**4b**) in the former, and 2-(2-methoxyphenyl)-*N*-propylbenzamide (**5a**) and 2-(4-methoxyphenyl)-*N*-propylbenzamide (**5b**) as well as a small amount of **2** in the latter. Product **2** was formed by hydrogen-atom abstraction from tetrahydrofuran by the diradical. The photolysis of **1** in the presence of *p*-xylene provided 2-(2,5-dimethylphenyl)-*N*-propylbenzamide (**6**) in a low yield of 41% and **2** in a higher yield. In the case of mesitylene, *N*-propyl-2-(2,4,6-trimethylphenyl)benzamide (**7**) was obtained in a trace amount and the corresponding arylated product for benzonitrile was not formed.



Scheme 2.

Märky et al. reported that the photolysis of 1-methylbenzotriazole gave arylated products, even in mesitylene and benzonitrile, in unexpected high yields comparable to the yield in benzene.[9] In the present case the low yields of **6** and **7** in *p*-xylene and mesitylene mean that plural methyl groups on the aromatic rings may prevent access to the diradical. We could not obtain acetophenone-added benzamide by acetophenone sensitization as well as benzonitrile-added benzamide by 254-nm irradiation. The existence of an electron-withdrawing group on the aromatic ring seems to decrease the reactivity with **1**. Iminocyclohexadienylidene has been reported to have the character of a zwitter ion.[8,18] The dipolar character of the diradical produced from **1** may be further enhanced by a carbonyl group (Scheme 2). This increases the positive charge at the 2-position of the ring in the diradical, suppressing the addition of benzonitrile or acetophenone to that position, because an inductive effect by electron-withdrawing groups causes electron defects at the ortho and para positions of the aromatic ring.

Experimental

The NMR spectra were measured on a JEOL GX-270 using TMS as an internal standard, and the mass spectra were measured by a JEOL JMS-SX102, respectively. The phosphorescence spectra was recorded with a Shimadzu F-3010 attached to a phosphorescence accessory.

Materials. Ethanol, benzene, cyclohexane, and tetrahydrofuran were reagent grade from Wako Pure Chemical Industries. Cyclohexane was used after purification by silica-gel chromatography. Tetrahydrofuran was distilled after reflux with sodium metal. The other two were used without purification. 2,3-Butanedione and anisole provided from Wako Pure Chemical Industry, and toluene, *p*-xylene, mesitylene, benzonitrile from Tokyo Kasei Kogyo Co. were purified by distillation. **1** was prepared from the alkylation of *o*-sulfobenzoic imide (Wako) by propyl iodide (Tokyo Kasei) and purified by vacuum distillation (mp 77—78 °C).

Preparative or General Irradiation of 1. The irradiation of 50 mg of **1** in ethanol and aromatic solvents was carried out in a 50 cm^3 quartz vessel with a 6-W low-pressure mercury lamp (Ushio ULO-6DQ) in a nitrogen atmosphere. Upon photochemical reactions with anisole, *p*-xylene, mesitylene, and benzonitrile which have higher boiling points, those aromatics were diluted to 5×10^{-2}, 1.4×10^{-1}, 2.2×10^{-1}, and 3.2×10^{-1} $mol\,dm^{-3}$, respectively, by tetrahydrofuran in order to facilitate removal of the reaction solutions under reduced pressure, where ca. 75% of the incident 254-nm light were absorbed by those aromatics. After evaporation of the solvent, the residue was separated by thin-layer chromatography of Kieselgel (PF254, Merck) by elution with a mixture of petroleum ether and diethylether. We could isolate **4a** from **4b**, and **5a** from **5b**, but did not succeed in separating the corresponding photoproducts produced in other *N*-alkyl-*o*-sulfobenzoic imides. For example, the mixture of *N*-ethyl-2-(2-methylphenyl)benzamide and *N*-ethyl-2-(4-methylphenyl)benzamide obtained upon the irradiation of *N*-ethyl-*o*-sulfobenzoic imide in toluene was hardly separated.

2-(2-Methylphenyl)-*N*-propylbenzamide (4a). Mp 62—63 °C (from hexane); IR (KBr) 3300 (NH), 1635 cm^{-1} (CO); $^1H\,NMR$ ($CDCl_3$) $\delta=0.65$ (3H, t, $J=7.3$ Hz, CH_3), 1.21 (2H, sex, $J=7.3$ Hz, $CH_2C\underline{H}_2CH_3$), 2.38 (3H, s, CH_3 on ring), 3.11 (2H, m, $NHC\underline{H}_2CH_2$), 5.23 (1H, br, NH), 7.2—7.7 (8H, m, ArH). MS *m*/*z* 253 (M^+). Found: C, 80.17; H, 7.60; N, 5.43%. Calcd for $C_{17}H_{19}NO$: C, 80.59; H, 7.56; N, 5.53%.

2-(4-Methylphenyl)-*N*-propylbenzamide (4b). Oily; IR (neat) 3210 (NH), 1650 cm^{-1} (CO); $^1H\,NMR$ ($CDCl_3$) $\delta=0.64$ (3H, t, $J=7.3$ Hz, CH_3), 1.10 (2H, sex, $J=7.3$ Hz, $CH_2C\underline{H}_2CH_3$), 2.12 (3H, s, CH_3 on ring), 3.06 (2H, m, $NHC\underline{H}_2CH_2$), 5.30 (1H, br, NH), 7.2—7.9 (8H, m, ArH). MS *m*/*z* 253 (M^+).

2-(2-Methoxyphenyl)-*N*-propylbenzamide (5a). Mp 91—92 °C (from hexane); IR (KBr) 3240 (NH), 1640 cm^{-1} (CO); $^1H\,NMR$ ($CDCl_3$) $\delta=0.67$ (3H, t, $J=7.3$ Hz, CH_3), 1.20 (2H, sex, $J=7.3$ Hz, $CH_2C\underline{H}_2CH_3$), 3.10 (2H, m, $NHC\underline{H}_2CH_2$), 3.76 (3H, s, OCH_3), 5.57 (1H, br, NH), 6.94 (1H, d, $J=8.2$ Hz, 3′H), 7.03 (1H, t, $J=7.8$ Hz, 5′H), 7.2—7.8 (6H, ArH). MS *m*/*z* 269 (M^+). Found: C, 75.51; H, 7.11; N, 5.11%. Calcd for $C_{17}H_{19}NO_2$: C, 75.80; H, 7.06; N, 5.20%.

2-(4-Methoxyphenyl)-*N*-propylbenzamide (5b). Mp 75—76 °C (from hexane); IR (KBr) 3210 (NH), 1650 cm^{-1} (CO); $^1H\,NMR$ ($CDCl_3$) $\delta=0.68$ (3H, t, $J=7.3$ Hz, CH_3), 1.26 (2H, sex, $J=7.3$ Hz, $CH_2C\underline{H}_2CH_3$), 3.14 (2H, m, $NHC\underline{H}_2CH_2$), 3.84 (3H, s, OCH_3), 5.25 (1H, br, NH), 6.95 (2H, d, $J=8.9$ Hz, 3′H, 5′H), 7.2—7.7 (6H, ArH). MS *m*/*z* 269 (M^+). Found: C, 75.70; H, 7.12; N, 5.12%. Calcd for $C_{17}H_{19}NO_2$: C, 75.80; H, 7.06; N, 5.20%.

2-(2,5-Dimethylphenyl)-*N*-propylbenzamide (6). Oily; IR (neat) 3310 (NH), 1650 cm^{-1} (CO); $^1H\,NMR$ ($CDCl_3$) $\delta=0.64$ (3H, t, $J=7.3$ Hz, CH_3), 1.08 (2H, sex, $J=7.3$ Hz, $CH_2C\underline{H}_2CH_3$), 2.06 (3H, s, CH_3 on ring), 2.34 (3H, s, CH_3 on ring), 3.06 (2H, m, $NHC\underline{H}_2CH_2$), 5.35 (1H, br, NH), 7.2—7.7 (7H, ArH). MS *m*/*z* 267 (M^+).

***N*-Propyl-2(2,4,6-trimethylphenyl)benzamide (7).** Mp 101 °C (from hexane); IR (KBr) 3250 (NH), 1640 cm^{-1} (CO); $^1H\,NMR$ ($CDCl_3$) $\delta=0.65$ (3H, t, $J=7.4$ Hz, CH_3), 1.14 (2H, sex, $J=7.2$ Hz, $CH_2C\underline{H}_2CH_3$), 1.97 (6H, s, CH_3 on ring), 2.34 (3H, s, CH_3 on ring), 3.08 (2H, m, $NHC\underline{H}_2CH_2$), 5.35 (1H, br, NH), 6.92—8.2 (6H, ArH). MS *m*/*z* 281 (M^+).

Quantum Yield Determination. Quantum-yield measurements were carried out upon the irradiation of 254-nm or 366-nm light from a USH-500D lamp to a deaerated solution of **1** in a quartz cylindrical cell. The 254-nm line was isolated through the combination of a $NiSO_4$ solution and a 1,4-diphenyl-1,3-butadiene solution with a UVD-33 filter. The 366-nm line was selected with the aid of Toshiba cutoff filters (UV-35 and UV-D33S), and, accordingly, all exciting light shorter than 350 nm was removed. The light intensity was determined by means of the usual method using a potassium trioxalatoferrate(III) actinometer. The amounts of **2** and **3** were determined by means of the HPLC method (Shimadzu LC-10A system) by passing a mixture of methanol and water as an eluent through an ODS-2 column at 30 °C.

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