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The Photolysis of *N,O*-Diacyl-*N*-phenylhydroxylamines[1]

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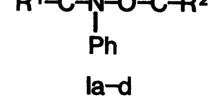
The photochemical decomposition of the title compounds yielded the rearrangement products derived from 1,3- and 1,5-aroyloxyl migrations in addition to the fragmentation products typical of the aroyloxyl and amido radicals, while only 1,3-aroyloxyl migration was observed on thermolysis. The results of crossover experiments indicate an intramolecular rearrangement, probably involving homolysis of the N-O bond in the excited states. Triplet quenching studies demonstrate that the rearrangement and fragmentation proceed exclusively *via* the first excited singlet state. No formation of the rearrangement products on triplet sensitization was explained on the basis of the spin multiplicity effects on a radical-radical recombination process within a solvent cage.

The elegant and pioneering works of Ochiai and his coworkers in the field of the chemistry of heteroaromatic amine *N*-oxides have greatly stimulated mechanistic investigations of the reactions between these *N*-oxides and acylating agents.[2] The devotion of many workers to this mechanistic study has resolved many questions concerning the mechanism of the reactions, which heteroaromatic and aromatic amine *N*-oxides undergo, and led to the syntheses of many biochemically and pharmaceutically important compounds.[3] In connection with the rearrangements of *O*-acylated amine *N*-oxides, the acyloxyl migration of *N,O*-diacyl-*N*-arylhydroxylamines has attracted much attention mainly because these *N*-arylhydroxylamines have a closely related structure to "anhydrobase" which is a key intermediate for the rearrangement reactions of tertiary amine *N*-oxides.[4]

In addition, mechanistic studies of *N,O*-diacyl-*N*-arylhydroxylamines[5] have contributed to clarifying the mode of the N-O bond cleavage that has been a question of controversy for a long time in the rearrangement of heteroaromatic *N*-oxides and related compounds.[6] Based on both kinetic and oxygen-18 tracer studies it was suggested that the electronic effects on the heterolysis of the N-O bond play a crucial role in determining the mechanism of 1,3-rearrangement.[5f] However, it is difficult to exclude completely the possibility of a radical rearrangement *via* the homolysis of the N-O bond although the rearrangement is now believed to proceed *via* the exclusive heterolytic cleavage of the N-O bond.[6,7]

On the other hand, Walling and Naglieri have found that the photolysis of *N,O*-diacylhydroxylamines gives the products derived from the homolysis of the N-O bond.[8] Their work suggested us that a systematic study of the photolysis of *N,O*-diacyl-*N*-arylhydroxylamines would lead to a new information on the mechanism of acyloxyl migrations of these hydroxylamines and related compounds. Because there are only a few investigations of the photochemical rearrangement of hydroxamic acid derivatives,[9] we have prepared *N,O*-diacyl-*N*-phenylhydroxylamines (**Ia—d**) and examined their photochemical behavior, hoping to gain further insight into the mechanism of acyloxyl migration. In this paper we present the first observation of photorearrangements of **Ia—d** and discuss the mechanism of the photolysis of these hydroxylamines.



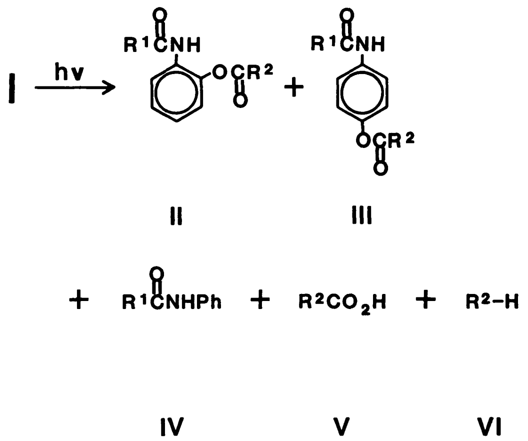
$R^1\text{-}C(=O)\text{-}N(Ph)\text{-}O\text{-}C(=O)\text{-}R^2$

Ia–d

Ia: R^1=1-naphthyl (1-Np), R^2=p-tolyl (p-Tl)
Ib: R^1=p-Tl, R^2=1-Np
Ic: R^1=R^2=1-Np
Id: R^1= R^2= p-Tl

Results and Discussion

*Products from the Photolyses of **Ia—d**.* An oxygen-free acetonitrile solution of **I** was irradiated with Pyrex-filtered light. The irradiation was done in a water bath so that the reaction temperature was maintained constant during the photolysis (23±1 °C). Each of reactions gave two rearrangement products **II** and **III** together with arenecarboxanilide **IV**, carboxylic acid **V**, and hydrocarbon **VI** as summarized in Table 1.



These products were identified by comparing their HPLC behavior at two different wavelengths (230 and 270 nm) with that of independently prepared authentic samples. In addition to the HPLC peaks of **II—VI** one can see some unknown peaks on the chromatogram, which will be discussed in a later section. Starting

TABLE 1. PHOTOLYSIS OF **Ia—d** (0.0066 M) IN ACETONITRILE

Compound	Irradiation time/min	Conversion/%	HPLC yield[a] of product/%				
			II	**III**	**IV**	**V**	**VI**
Ia	15	40.0	4.4	1.5	1.5	10.0	—[b]
	60	85.5	7.3	2.1	5.5	24.0	—[b]
	240	98.4	9.0	2.4	10.2	29.6	8[c]
Ib	15	43.2	0.3	0.1	2.8	11.0	—[b]
	60	71.9	1.1	1.6	8.6	31.5	—[b]
	240	97.3	0.8	0.5	28.4	64.8	3
Ic	15	27.3	1.5	1.5	2.3	17.7	—[b]
	30	48.6	3.0	2.5	5.5	33.5	—[b]
	180	94.7	2.8	2.1	21.2	70.2	3
Id	30	33.4	5.2	3.2	3.3	13.5	—[b]
	60	45.9	7.4	2.7	6.2	22.1	—[b]
	240	75.6	10.2	2.8	15.2	53.3	7[c]

a) Based on starting hydroxylamines. b) Not determined. c) GLC yield.

TABLE 2. CROSSOVER EXPERIMENTS IN ACETONITRILE[a]

Compound	Conversion/%	Rearrangement product and its HPLC yield[b]/%							
		IIc	**IIIc**	**IId**	**IIId**	**IIa**	**IIIa**	**IIb**	**IIIb**
		crossover product							
Ia **Ib**	94.8 79.9	0.03	—[c]	0.01	0.01	4.2	—[d]	1.7	—[e]
						crossover product			
Ic **Id**	78.9 60.8	—[f]	2.4	1.5	2.4	0.03	—[f]	0.02	0.03

a) The initial concentrations of **Ia—d** were all 0.0066 M. Deaerated solutions were irradiated for 2 h with Pyrex-filtered light in a water bath (20±1 °C). b) Based on starting hydroxylamines. c) Could not be determined because of overlapping with the HPLC peak of starting **Ia**. d) The HPLC peak of starting **Ib** made this yield determination impossible. e) Could not be determined because of overlapping with unknown HPLC peak(s) derived from **Ia**. f) The HPLC peak of starting **Id** interfered with exact evaluation of this yield.

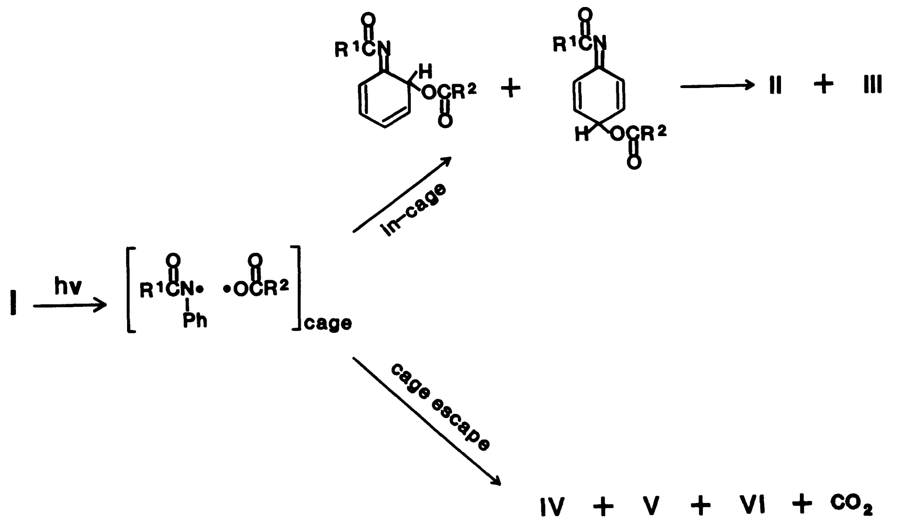
hydroxylamines **Ia—d** were recovered quantitatively without the irradiation, of course. To get more unambiguous proof of the structure for the photoproducts, irradiation of one of the starting hydroxylamines **Ia** was continued under the same conditions as above until disappearance of **Ia** was complete (monitored by TLC). Chromatography of the photolyzate allowed isolation and identification of **IIa** (4%, isolated yield), **IIIa** (8%), **IVa** (20%), **Va** (10%), and **VIa** (9%, GLC yield) except carbon dioxide (about 30%) which was characterized as barium carbonate. This product distribution is qualitatively consistent with that obtained by HPLC analysis of the photolyzate. We obtained also tarry product mixtures from which attempts to isolate any crystalline materials were not fruitful.

Independent irradiation of the photoproducts clearly shows that the rearrangement and fragmentation products undergo undesirable photodecompositions to different extent depending on the structure of the products (**IIa**, **IId**, and **IIIb**, 30% decomposition on 2 h irradiation; **IIIa** and **IIId**, 40—50%; **IIb**, **IIc**, and **IIIc**, 70—80%; **IV**, **V**, and **VI**, 2—7%). The decomposition of the fragmentation products during the irradiation is minor, whereas that of the rearrangement products takes place remarkably. Thus the low yields of **II** and **III**, especially **IIb**, **IIc**, and **IIIc**, may be ascribed in part to this low photostability.

Crossover Experiment and Thermolysis. To ascertain the intra- or intermolecularity of this interesting photorearrangement, an equimolar mixture of **Ia** and **Ib** in acetonitrile was irradiated with Pyrex-filtered light in the same manner. Careful HPLC analysis of the photolyzate indicates the formation of negligible amounts of the crossover products (**IIc**, **d**, and **IIIc**, **d**) in addition to the noncrossover rearrangement products (**IIa**, **b**, and **IIIa**, **b**) (see Table 2). A similar finding was obtained also on irradiation of a mixture of **Ic** and **Id**. These findings demonstrate that the photorearrangements proceed by an exclusively intramolecular aroyloxyl shift.

Since the photoreactions of **Ia—d** are formally analogous to the photo-Fries reactions that proceed through a caged radical mechanism in solution,[10] it is reasonable to assume that the photolysis of these hydroxylamines involves homolytic cleavage of the N-O bond in an excited state forming the amido and aroyloxyl radicals, which either recombine within a solvent cage to afford the rearrangement products or escape out of the cage to give the fragmentation products by hydrogen abstraction from the solvent or otherwise as shown in Scheme 1. The homolysis of the N-O bond is supported by the facts that the products derived from the amido and aroyloxyl radicals were identified, and that *N*,*O*-diacylhydroxylamines, whose structure is very similar to that of **Ia—d**, undergo the homolytic photolysis.[8]

In order to examine possible involvement of hetero-



Scheme 1.

lysis of the N-O bond, **Ia**—**d** were heated at 120—130 °C in dimethyl sulfoxide. If participation of an ionic mechanism would be responsible for the formation of **II** and **III**, the same rearrangement products should be obtained thermally because the rearrangement of closely related *N,O*-diacyl-*N*-arylhydroxylamines is well known to proceed through the heterolytic scission of the N-O bond.[5] As seen from Table 3 the thermolyses gave only the ortho-migrated products **II** accompanied by the recovered starting materials, whereas neither fragmentation nor migration of an aroyloxyl group to the para-position could be observed. Clearly the products of the photolysis are quite different from those of the thermal decomposition, indicating that at least the para-migrated rearrangement and fragmentation products originate from the homolytic cleavage of the N-O bond. The fact that the N-O bond of diacylhydroxylamines readily undergoes homolytic cleavage in the excited states[8] allows us to propose a radical mechanism to account for the formation of **II** as well as **III**—**VI**.

Solvent Effects on the Photolysis of ***Ia***. A free radical mechanism requires that anilide **IV** and carboxylic acid **V** should be found in comparable amounts because of the minor process of decarboxylation giving eventually either toluene or naphthalene. Table 1 shows, however, that there are always lower yields of **IV** than those of **V** at any conversion irrespective of the structure of starting hydroxylamines. This observation leads us to speculate that hydrogen abstraction to yield **IV** is not the only reaction pathway for the amido radical in acetonitrile. It is likely that hydrogen abstraction of the photochemically generated amido radical competes with such processes as dimerization, disproportionation, and addition[11] owing to the relatively low reactivity of acetonitrile toward hydrogen abstraction. These competing pathways might be responsible for the observation of some unknown HPLC peaks. We felt that solvent effects on the rearrangement and fragmentation pathways may clarify this point. The hydroxylamine **Ia** was chosen for this purpose. The results are given in Table 4. As expected the fragmentation products **IV** and **V** are found in comparable yields in 1,2-dichloroethane whose hydrogen atoms seem much more reactive to hydrogen abstraction compared with other two solvents used. In addition, some unknown HPLC peaks, which were observed in the photolysis in acetonitrile and benzene, could not be detected on the HPLC chromatogram of the photolyzate in 1,2-dichloroethane, supporting the view mentioned above.

Table 3. Thermolysis of **Ia**—**d** in dimethyl sulfoxide at 120—130 °C

Compound	Reaction time/h	Conversion/%	Yield[a] of product/% II	III
Ia	9	16	11	—[b]
Ib	10	88	65	—[b]
Ic	9	49	39	—[b]
Id	9	57	48	—[b]

a) Based on starting hydroxylamines. b) Not detected.

Quenching and Sensitization Experiments. *N,O*-Diacyl-*N*-phenylhydroxylamines used in this work exhibit a fluorescence with maxima between 370 and 390 nm except **Id** whose fluorescence is too weak to be observed. We estimated the first singlet excitation energy (E_S) of **Ia**—**c** from the absorption and fluorescence spectral data to tabulate in Table 5. The phosphorescence of **Ia**—**c** with 0,0 bands around 490 nm could be detected in acetonitrile at 77 K, while **Id** shows a broad phosphorescence at 422 nm. Table 5 also includes the first triplet excitation energy (E_T) estimated from the 0,0 bands of **Ia**—**c** and the emission maximum of **Id**. In Fig. 1 are typically shown the absorption and emission spectra of **Ia** in acetonitrile.

The phosphorescence of **Ia**—**d** (2×10^{-4} M, 1 M=1 mol dm^{-3}) is quenched by 1,3-cyclohexadiene (0.01 M), showing that this diene becomes a good triplet quencher in view of endothermicity of singlet-singlet energy transfer from **I** to the diene. Sensitization of the phosphorescence of **Ia**—**d** (2×10^{-4} M) by benzo-

Table 4. Solvent effects on the photolysis of **Ia**

Solvent	Irradiation time/min	Conversion/%	HPLC yield[a)] of product/%			
			IIa	**IIIa**	**IVa**	**Va**
Benzene	15	42.8	5.3	1.3	3.0	18.1
	30	71.6	7.3	2.4	7.6	37.6
	120	99.9	7.0	3.2	24.3	56.4
CH_2ClCH_2Cl	15	42.7	5.1	1.2	22.0	20.1
	30	80.9	7.4	1.8	41.7	42.7
	120	100	7.8	2.0	55.8	61.0

a) Based on starting hydroxylamines.

Table 5. The first singlet (E_S) and triplet (E_T) excitation energies of **Ia—d**, 1,3-cyclohexadiene, and benzophenone

(1 kcal=4.18 kJ)

Compound	E_S/kcal mol^{-1}	E_T/kcal mol^{-1}
Ia	90	59
Ib	86	58
Ic	85	58
Id	<97[a)]	68
1,3-Cyclohexadiene	97[b)]	52.4[b)]
Benzophenone	74.4[b)]	69.2[b)]

a) Estimated from a comparison of the absorption spectrum of **Id** with that of 1,3-cyclohexadiene. b) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, N. Y. (1973), p. 3.

phenone (2×10^{-3} M) was observed accompanying the quenching of sensitizer's phosphorescence (Fig. 2). This finding indicates benzophenone to be an excellent triplet sensitizer. Also in this case singlet-singlet energy transfer from sensitizer to **I** is endothermic. In order to decide whether the photolysis occurs from the excited singlet or triplet state, triplet quenching (313-nm light) and sensitization (mostly 366-nm light) experiments were performed. The results are summarized in Tables 6 and 7. Evidently, neither product formation nor disappearance of starting hydroxylamines was affected by 1,3-cyclohexadiene within the limits of experimental accuracy (Table 6), suggesting that the rearrangement and fragmentation products come from the reaction in the excited singlet state.[12)]

The diacylhydroxylamines **Ia—d** undergo greatly accelerated photodecompositions in the presence of benzophenone (Table 7). The fragmentation products are formed by the sensitized photolysis in which no benzophenone was consumed within the experimental error, whereas benzophenone does not sensitize the rearrangement. The finding that the triplet state photolysis gives the rearrangement products in a negligible yield is compatible with the result of triplet quenching experiment. Irradiation of the photoproducts **II—VI** with 366-nm light resulted in their negligible decomposition (less than 5% on 15 min irradiation) in the presence of the sensitizer (0.05 M). Another prominent facet in this triplet sensitization is that the yields of **IVa—c** are much low even at high conversion of **Ia—c**. The increased intensity of unknown HPLC peaks compensates for this decreased yield of anilide **IV**. Thus the fragmentation products including **IV** are undoubtedly formed by the sensitized photolysis.

Mechanism of the Photolyses. The triplet quenching and sensitization results establish that the rearrangement takes place *via* the excited singlet state, whereas the fragmentation products are obtained from both the excited singlet and triplet state reactions. As already noted the direct photolysis of **I** causes the homolytic scission of the N–O bond in the molecule

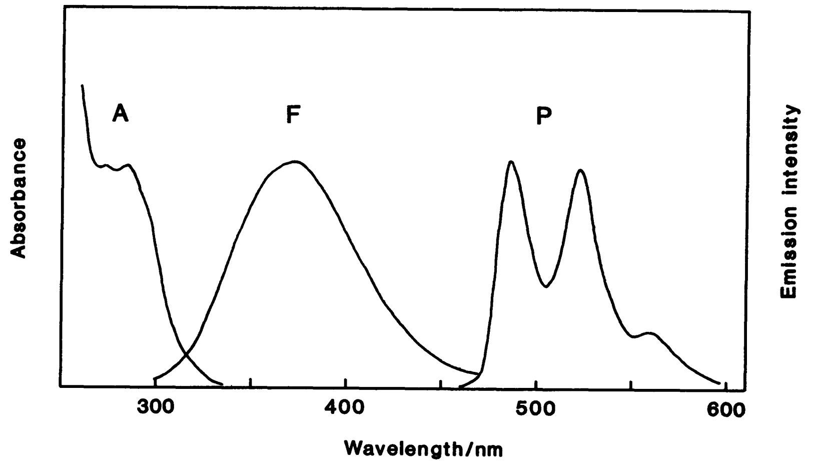


Fig. 1. UV absorption and emission spectra of **Ia** (2×10^{-4} M) in acetonitrile. (A): Absorption at room temperature; (F): Fluorescence at room temperature, excitation wavelength=315 nm; (P): Phosphorescence at 77 K, excitation wavelength=310 nm. Intensities have been adjusted for the sake of clarity.

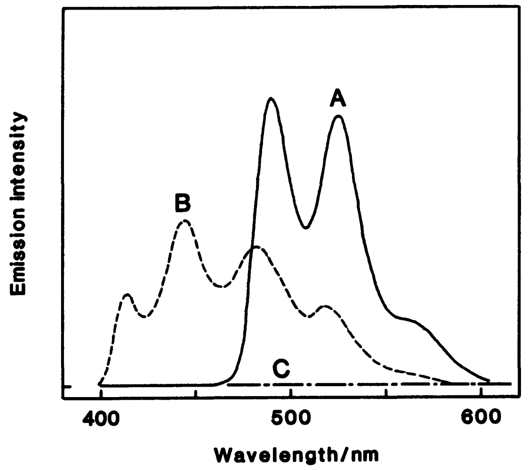


Fig. 2. Sensitization of the phosphorescence of **Ia** by benzophenone in acetonitrile at 77 K. (A): Sensitized phosphorescence of **Ia**, excitation wavelength=380 nm; [**Ia**]=2×10^{-4} M, [benzophenone]=2×10^{-3} M; (B) and (C): Phosphorescence of benzophenone (B) and **Ia** (C) under the same conditions.

affording the caged singlet radical pairs which undergo efficient cage reactions to give the rearranged products **II** and **III**, in competition with escape from the solvent cage (Scheme 2).

Since the rate of escape of the triplet radical pairs from the cage should be faster than the rate of the triplet→singlet intersystem crossing in the radical pairs,[13,14] no rearrangement products are formed by the triplet sensitized photolysis of **I**. Thus the sensitized reaction leads to the exclusive formation of "out-of-cage" reaction products as shown in Scheme 2, being consistent with the conviction that triplet radical pairs, in general, undergo very inefficient cage reactions.[15]

Experimental

All melting points were uncorrected. IR spectra were recorded on a Hitachi EPI-G3 infrared spectrometer. ^{1}H NMR spectra were obtained on a JEOL model PS-100 100 MHz spectrometer with TMS as an internal standard. UV and emission spectral data were collected with a Shimadzu UV-210 A spectrophotometer and a Shimadzu RF-500 spectrophotofluorimeter, respectively. Phosphorescence spectra were taken with a cylindrical rotating sector at 77 K. GLC analysis was carried out on a Hitachi 063 gas chromatograph using 2-m column packed with 10% Silicone SE-30 on Uniport B (60/80 mesh, Gasukuro Kogyo Inc.). HPLC separation of the photoproducts was performed on a Hitachi 638-50 high performance liquid chromatography apparatus with a 2.6×500-mm ODS (Hitachi gel #3050) column.

Table 6. Quenching of the photolysis of **Ia—d** by 1,3-cyclohexadiene (CHD) in acetonitrile

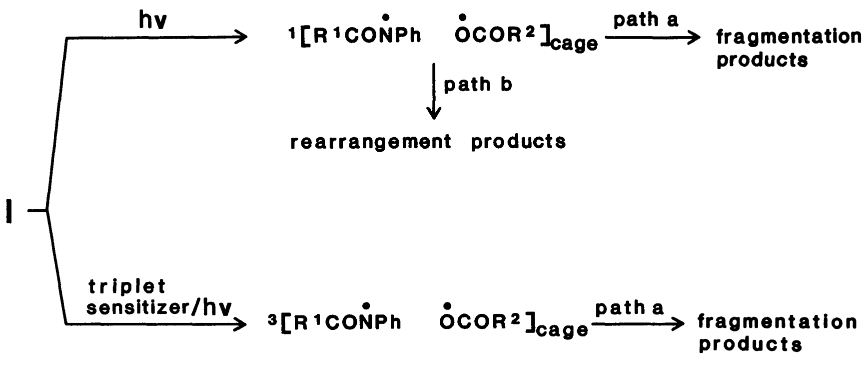
Compound	Irradiation time/min	Quencher	Conversion/%	HPLC yield$^{a)}$ of product/%			
				II	III	IV	V
Ia	60	none	13.9	4.2	1.2	0.5	3.9
	60	CHD	11.5	3.5	1.1	—$^{b)}$	2.0
	120	none	22.4	6.4	1.8	1.1	6.4
	120	CHD	26.2	6.2	1.8	—$^{b)}$	3.9
Ib	120	none	16.3	0.9	0.9	3.2	8.5
	120	CHD	17.9	1.2	1.2	2.9	6.8
	240	none	24.0	2.6	1.2	4.3	13.5
	240	CHD	26.8	2.9	1.4	5.6	13.1
Ic	60	none	11.3	0.3	0.5	1.2	8.2
	60	CHD	11.5	0.3	0.8	—$^{b)}$	6.5
	120	none	23.6	2.3	0.6	2.4	17.5
	120	CHD	18.7	2.6	1.2	—$^{b)}$	14.3
Id	60	none	10.2	2.1	1.5	1.2	5.3
	60	CHD	9.7	2.4	1.5	1.8	3.0
	120	none	19.1	4.0	2.3	2.4	6.7
	120	CHD	21.0	3.4	2.0	3.0	4.1

a) Based on starting hydroxylamines. b) Could not be determined because of overlapping with the HPLC peak of the quencher. No attempt to determine the yield of **VI** was made.

Table 7. Sensitization of the photolysis of **Ia—d** by benzophenone (BP) in acetonitrile

Compound	Irradiation time/min	Sensitizer	Conversion/%	HPLC yield$^{a)}$ of product/%				
				II	III	IV	V	VI
Ia	15	none	10.3	1.0	1.0	1.3	7.3	—$^{b)}$
	15	BP	96.1	$<1^{c)}$	$<1^{c)}$	3.3	33.5	$10^{d)}$
Ib	15	none	9.6	0.8	0.5	2.1	6.7	—$^{e)}$
	15	BP	65.3	0.2	$<0.5^{c)}$	2.1	44.8	—$^{e)}$
Ic	15	none	22.3	1.1	0.6	1.0	12.3	—$^{b)}$
	15	BP	83.1	$<1.1^{c)}$	$<0.6^{c)}$	1.9	55.1	1
Id	15	none	4.0	1.5	0.9	0.6	1.9	—$^{e)}$
	15	BP	43.0	0.2	$<0.9^{c)}$	14.4	10.0	—$^{e)}$

a) Based on starting hydroxylamines. b) Could not be detected. c) Could not be determined accurately because of either too small HPLC peak or of overlapping with unknown small peak(s) arising from the sensitized photolysis. d) GLC yield. e) Not determined.



path a, 'out-of-cage' reaction; path b, 'in-cage' reaction

Scheme 2.

Materials. Acetonitrile was purified according to the modified procedure of Walden and Birr.[16] Benzene and 1,2-dichloroethane (spectrograde from Dojin Chemical Inc.) were used without further purification. Acetonitrile and water (HPLC grade from Wako Pure Chemical Industries, Ltd.) were used as received for HPLC analysis. 1,3-Cyclohexadiene (Aldrich Chemical Co.) was fractionally distilled prior to use and stored in a refrigerator. Benzophenone (reagent grade, Wako) was purified by column chromatography over silica gel (70/230 mesh) followed by repeated recrystallization from aqueous ethanol. 1-Naphthoic and *p*-toluic acids (reagent grade, Wako) were recrystallized from benzene and aqueous ethanol, respectively. Naphthalene (reagent grade, Wako) was purified by sublimation at reduced pressure. Toluene (spectrograde, Dojin) was used as received.

Preparation of Starting N,O-*Diacyl*-N-*phenylhydroxylamines* (**Ia—d**). *N*-Phenylhydroxylamine was prepared by the reduction of nitrobenzene with zinc dust in water containing ammonium chloride, then recrystallized from hexane, mp 80.5—81.5 °C (lit,[17] 81 °C). *N*-(*p*-Toluoyl)-*N*-phenylhydroxylamine was obtained from the reaction of *p*-toluoyl chloride with two equiv of *N*-phenylhydroxylamine in ether with stirring in an ice bath. After the usual workup which consisted of washing the reaction mixture with water, drying the ethereal solution over $MgSO_4$, and removing the solvent on a rotary evaporator, recrystallization of the crude product from benzene–hexane gave colorless crystals, mp 121—122 °C; IR (KBr) 3200 and 1610 cm^{-1}. *N*-(1-Naphthoyl)-*N*-phenylhydroxylamine was prepared similarly from the reaction of 1-naphthoyl chloride with two equiv of *N*-phenylhydroxylamine, then recrystallized from benzene–hexane, mp 129—130 °C; IR (KBr) 3220 and 1620 cm^{-1}. The reactions of these *N*-aroyl-*N*-phenylhydroxylamines with the corresponding aroyl chlorides in the presence of pyridine in dichloromethane gave **Ia—d** whose physical properties are the followings.

N-*(1-Naphthoyl)*-O-*(*p-*toluoyl)*-N-*phenylhydroxylamine* (**Ia**). Mp 134.5—135.5 °C (from benzene–hexane); NMR ($CDCl_3$) δ=2.36 (3H, s), 7.08—7.90 (15H, m), and 8.36 (1H, d, J=8 Hz); IR (KBr) 1750 and 1680 cm^{-1}. Found: C, 79.19; H, 4.94; N, 3.73%. Calcd for $C_{25}H_{19}NO_3$: C, 78.74; H, 4.99; N, 3.67%.

N-*(*p-*Toluoyl)*-O-*(1-naphthoyl)*-N-*phenylhydroxylamine* (**Ib**). Mp 164—165 °C (from benzene–hexane); NMR ($CDCl_3$) δ= 2.30 (3H, s), 7.00—8.22 (15H, m), and 8.74 (1H, d, J=8 Hz); IR (KBr) 1775 and 1690 cm^{-1}. Found: C, 79.11; H, 4.99; N, 3.71%. Calcd for $C_{25}H_{19}NO_3$: C, 78.74; H, 4.99; N, 3.67%.

N,O-*Di(1-naphthoyl)*-N-*phenylhydroxylamine* (**Ic**). Mp 116—117 °C (from benzene–hexane); NMR ($CDCl_3$) δ=7.12—8.02 (17H, m), 8.40 (1H, d, J=8 Hz), and 8.70 (1H, d, J=8 Hz); IR (KBr) 1740 and 1670 cm^{-1}. Found: C, 80.99; H, 4.59; N, 3.37%. Calcd for $C_{28}H_{19}NO_3$: C, 80.58; H, 4.56; N, 3.36%.

N,O-*Di(*p-*toluoyl)*-N-*phenylhydroxylamine* (**Id**). Mp 122—123 °C (from benzene–hexane); NMR ($CDCl_3$) δ=2.26 (3H, s), 2.36 (3H, s), 6.96 (2H, d, J=8 Hz), 7.14—7.48 (9H, m), and 7.90 (2H, d, J=8 Hz); IR (KBr) 1760 and 1660 cm^{-1}. Found: C, 76.82; H, 5.52; N, 4.03%. Calcd for $C_{22}H_{19}NO_3$: C, 76.52; H, 5.51; N, 4.06%.

Photolyses of **Ia—d**. A nitrogen purged solution of **I** (0.0066 M) in acetonitrile, benzene, or 1,2-dichloroethane (10 mL), which was placed in a sealed Pyrex tube, was irradiated for a given period of time with a 400 W high pressure mercury lamp set in a Pyrex cooling jacket. Parallel irradiations of the solutions were done on a merry-go-round apparatus (Riko model RH400-10W) immersed into a water bath (23±1 °C). The photolyzate thus obtained were subjected to the HPLC analysis. The yields of the products were determined by employing the linear calibration curves made for each product under the same analytical conditions. For the purpose of isolating the photoproducts a solution of **Ia** (0.0087 M) in acetonitrile (300 mL), placed in a Pyrex vessel, was irradiated for 70 min under purified and dried nitrogen with a Pyrex-filtered 400 W high pressure mercury lamp. After evaporation of the solvent, the resulting residue was chromatographed on silica gel (230 mesh, Merck) eluting with benzene and then with chloroform. This separation procedure allowed isolation and identification of **IIa**, **IIIa**, and **IVa**, whose structures were determined by comparing their physical properties with those of authentic samples prepared independently. In another experiment the photolyzate concentrated *in vacuo* was extracted with a 5% sodium hydrogencarbonate solution (50 mL). The extract was washed with dichloromethane twice and then acidified to pH 2 with 4M HCl giving *p*-toluic acid as a white solid. The carbon dioxide formed by this photolysis was introduced into a 0.1 M $Ba(OH)_2$ (150 mL) after having been passed through a cold trap by a nitrogen stream. The precipitate $BaCO_3$ was removed by quick filtration and the filtrate was titrated with 0.1 M HCl. The failure to avoid contamination with carbon dioxide in the air during this procedure resulted in overestimation of the yield of photochemically generated carbon dioxide. In order to detect toluene as a product a nitrogen purged acetonitrile solution of **Ia** (0.052 M) in a sealed Pyrex tube was irradiated for 4 h. The photolyzate was submitted for the GLC analysis that led to identification of toluene whose yield was estimated by a linear calibration curve.

Thermolyses of ***Ia—d.*** A nitrogen purged dimethyl sulfoxide solution of **I** (2 mmol) in a sealed ampule was heated at 120—130 °C in an oil bath for a given period of time. The reaction mixture was poured onto water (100 mL) and extracted three times with chloroform. The combined chloroform extracts were washed twice with water and then dried over Na_2SO_4. Removal of the solvent on a rotary evaporator gave the solid residue from which **II** was isolated along with the starting **I** by column chromatography over silica gel (70/230 mesh, Merck) with benzene–chloroform (1:1 v/v) as eluent.

*Preparation of Authentic Samples (**II**, **III**, and **IV**).* *N*-(*p*-Toluoyl)-*o*-aminophenol and *N*-(1-naphthoyl)-*o*-aminophenol were prepared by *N*-aroylation of two equiv of *o*-aminophenol with *p*-toluoyl and 1-naphthoyl chlorides in dichloromethane, respectively. Recrystallization of the crude products from aqueous ethanol gave colorless crystals, mp (the former anilide) 157.5—158.5 °C; IR (KBr) 3410, 3080 (broad), and 1640 cm^{-1}. Mp (the latter anilide) 194.5—195.5 °C; IR (KBr) 3400, 3100 (broad), and 1640 cm^{-1}. *N*,*O*-Diacyl-*o*-aminophenols (**IIa—d**) were derived from the reactions between *N*-acyl-*o*-aminophenols and the corresponding acyl chlorides in the presence of triethylamine in dichloromethane or ether. Physical properties are the followings. *N*-(1-Naphthoyl)-*O*-(*p*-toluoyl)-*o*-aminophenol (**IIa**), mp 168—170 °C (from benzene–hexane); IR (KBr) 3180, 1730, and 1650 cm^{-1}. Found: C, 79.02; H, 4.96; N, 3.65%. Calcd for $C_{25}H_{19}NO_3$: C, 78.74; H, 4.99; N, 3.67%. *N*-(*p*-Toluoyl)-*O*-(1-naphthoyl)-*o*-aminophenol (**IIb**), mp 137—138 °C (from benzene–hexane); IR (KBr) 3430, 1735, and 1675 cm^{-1}. Found: C, 78.87; H, 4.92; N, 3.67%. Calcd for $C_{25}H_{19}NO_3$: C, 78.74; H, 4.99; N, 3.67%. *N*,*O*-Di(1-naphthoyl)-*o*-aminophenol (**IIc**), mp 177.5—178.5 °C (from benzene–hexane); IR (KBr) 3200, 1730, and 1640 cm^{-1}. Found: C, 80.95; H, 4.54; N, 3.36%. Calcd for $C_{28}H_{19}NO_3$: C, 80.58; H, 4.56; N, 3.36%. *N*,*O*-Di(*p*-toluoyl)-*o*-aminophenol (**IId**), mp 108.5—109.5 °C (from benzene–hexane); IR (KBr) 3270, 1735, and 1640 cm^{-1}. Found: C, 76.58; H, 5.53; N, 4.07%. Calcd for $C_{22}H_{19}NO_3$: C, 76.52; H, 5.51; N, 4.06%.

N-(*p*-Toluoyl)-*p*-aminophenol and *N*-(1-naphthoyl)-*p*-aminophenol were prepared by the reactions of two equiv of *p*-aminophenol with *p*-toluoyl and 1-naphthoyl chlorides in dichloromethane, respectively. These reactions were heterogeneous because of the low solubility of *p*-aminophenol so that vigorous stirring was required during the course of these acylations. The crude products were recrystallized from aqueous ethanol affording colorless crystals, mp (the former anilide) 212.5—214 °C; IR (KBr) 3380, 3320, and 1650 cm^{-1}. Mp (the latter anilide) 198.5—199 °C; IR (KBr) 3240, 3190, and 1605 cm^{-1}. *N*,*O*-Diacyl-*p*-aminophenols (**IIIa—d**) were prepared by treatment of *N*-acyl-*p*-aminophenols with the corresponding acyl chlorides in the presence of triethylamine in dichloromethane. These reactions were also heterogeneous. Physical properties are the followings. *N*-(1-Naphthoyl)-*O*-(*p*-toluoyl)-*p*-aminophenol (**IIIa**), mp 214—215 °C (from ethyl acetate); IR (KBr) 3270, 1730, and 1645 cm^{-1}. Found: C, 79.04; H, 5.03; N, 3.69%. Calcd for $C_{25}H_{19}NO_3$: C, 78.74; H, 4.99; N, 3.67%. *N*-(*p*-Toluoyl)-*O*-(1-naphthoyl)-*p*-aminophenol (**IIIb**), mp 235.5—236.5 °C (from ethyl acetate); IR (KBr) 3300, 1730, and 1650 cm^{-1}. Found: C, 78.95; H, 4.98; N, 3.67%. Calcd for $C_{25}H_{19}NO_3$: C, 78.74; H, 4.99; N, 3.67%. *N*,*O*-Di(1-naphthoyl)-*p*-aminophenol (**IIIc**), mp 190—191 °C (from ethyl acetate); IR (KBr) 3260, 1720, and 1645 cm^{-1}. Found: C, 80.85; H, 4.56; N, 3.38%. Calcd for $C_{28}H_{19}NO_3$: C, 80.58; H, 4.56; N, 3.36%. *N*,*O*-Di(*p*-toluoyl)-*p*-aminophenol (**IIId**), mp 245.5—246.5 °C (from ethyl acetate); IR (KBr) 3320, 1725, and 1645 cm^{-1}. Found: C, 76.71; H, 5.46; N, 4.10%. Calcd for $C_{22}H_{19}NO_3$: C, 76.52; H, 5.51; N, 4.06%.

1-Naphthanilide (**IVa**, **c**) and *p*-toluanilide (**IVb**, **d**) which were prepared by the reactions of 1-naphthoyl and *p*-toluoyl chlorides with two equiv of aniline in dichloromethane under usual conditions, respectively, had the following physical properties: **IVa**, **c**, mp 162—163 °C (from benzene); IR (KBr) 3270 and 1650 cm^{-1}. Found: C, 82.95; H, 5.26; N, 5.88%. Calcd for $C_{17}H_{13}NO$: C, 82.59; H, 5.26; N, 5.67%. **IVb**, **d**, mp 145—146 °C (from benzene); IR (KBr) 3330 and 1645 cm^{-1}. Found: C, 79.77; H, 6.19; N, 6.71%. Calcd for $C_{14}H_{13}NO$: C, 79.62; H, 6.16; N, 6.64%.

Triplet Quenching and Sensitization. Ten milliliters of an acetonitrile solution of **I** (0.0066 M) and either quencher (0.1 M) or sensitizer (0.05 M) was placed in a Pyrex tube, degassed by bubbling purified nitrogen through it for 10 min, and sealed. Deaerated solutions with and without these additives were irradiated in parallel for the same period of time on a merry-go-round apparatus with either 313- or 366-nm light through a Pyrex-cylindrical solution filter (1-cm in length, 6-cm in diameter, and 22-cm in height) from a 400 W high pressure mercury lamp. All the irradiations were carried out in a water bath whose temperature was kept constant during the photolysis by circulating water through it. The 313-nm light for quenching experiment was isolated with a potassium chromate (0.002 M) in a 1% aqueous solution of potassium carbonate. A solution of copper sulfate pentahydrate (250 g dm^{-3}) was used as the filter for sensitization experiment. The band passed had a 90% transmittance (T) at 366 nm and a 9% T at 313 nm. Molar absorption coefficients of **Ia**, **Ib**, **Ic**, and **Id** were estimated to be 1940, 6740, 9180, and 290 (M^{-1} cm^{-1}) at 313 nm, respectively, and 2.6, 2.8, 3.3, and 0.5 (M^{-1} cm^{-1}) at 366 nm, respectively, in acetonitrile at room temperature.

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