Photoreaction of 2-Halo-*N*-pyridinylbenzamide: Intramolecular Cyclization Mechanism of Phenyl Radical Assisted with n-Complexation of Chlorine Radical

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The photochemical behavior of 2-halo-*N*-pyridinylbenzamide (**1**−**4** in Chart 1) was studied. The photoreaction of 2-chloro-*N*-pyridinylbenzamides **1a**, **2a**, **3a**, and **4** afforded photocyclized products, benzo[*c*]naphthyridinones (**6**−**9** and **16**), in high yield, whereas the bromo analogues **1b**, **2b**, and **3b** produced extensively photoreduced products, *N*-pyridinylbenzamides (**1c**, **10**, and **11**), with minor photocyclized product. Since the photocyclization reaction of 2-chloro-*N*-pyridinylbenzamide is retarded by the presence of oxygen and sensitized by the presence of a triplet sensitizer, acetone or acetophenone, a triplet state of the chloro analogue is involved in the reaction. Since several radical intermediates, particularly n-complexes of chlorine radical, are identified in the laser flash photolysis of 2-chloro-*N*-pyridinylbenzamide, an intramolecular cyclization mechanism of phenyl radical assisted with n-complexation of chlorine radical for the cyclization reaction is proposed: the triplet state (78 kcal/mol) of the chloro analogue (**1a**), which is populated by the excitation of **1a** undergoes a homolytic cleavage of the C−Cl bond to give phenyl and chlorine radicals; while chlorine radical holds the neighbor pyridinyl ring with its n-complexation, the intramolecular arylation of the phenyl radical with the pyridinyl ring proceeds to produce a conjugated 2,3-dihydropyridinyl radical and then the conjugated radical aromatizes to afford a cyclized product, benzo[*c*]naphthyridinone by ejecting a hydrogen. The photoreduction product can be formed by hydrogen atom abstraction of the phenyl σ radical from the environment.

Introduction

Kharasch and Wolf described a synthesis of biphenyl by photoarylation of iodobenzene in benzene in 1961.[1] Since then, the intramolecular photoarylation has been widely applied to obtain cyclized molecular systems.[2] The photocyclization of aryl halide has been reviewed by Grimshaw and de Silva,[3] Kessar and Mankotia.[4a] The C−X bond cleavage in the photoreaction of aryl halide has been also scrutinized by Bunce.[4b]

The intramolecular photocyclization of aryl halide has been investigated in relation to the synthetic method and the reaction mechanism.[5] We have reported that heterocyclic molecular systems are formed from the photocyclization of haloarene tethered to arene by several linkages,[6] and a photohomolytic radical mechanism is involved in the photocyclization of *N*-phenylalkyl-2-halopyridinium and *N*-(2-halophenyl)alkylpyridinium salts.[7] In conjunction with the study of the heterocyclic ring formation, we recently and unexpectedly observed that photoreaction of *N*-(2-halophenyl)pyridinecarboxamide in a basic medium produced an intramolecular photosubstitution product, 2-pyridinylbenzoxazole instead of a photocyclization product,[8] whereas photoreaction of 2-chloro-*N*-pyridinylbenzamide (**1a** in Chart 1) in a weak basic or neutral medium afforded an intramolecular photocyclization product, benzo[*c*]naphthyridinone. These reactions are straightforward and valuable for the syntheses of heterocyclic compounds such as benzoxazole and benzonaphthyridinone derivatives. Thus, it is desirable to develop the synthetic methods of the

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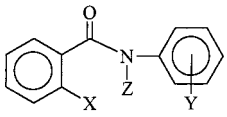
Chart 1



1a: X = Cl, Y = 4-N (4-pyridinyl), Z = H
1b: X = Br, Y = 4-N (4-pyridinyl), Z = H
1c: X = H, Y = 4-N (4-pyridinyl), Z = H
2a: X = Cl, Y = 3-N (3-pyridinyl), Z = H
2b: X = Br, Y = 3-N (3-pyridinyl), Z = H
3a: X = Cl, Y = 2-N (2-pyridinyl), Z = H
3b: X = Br, Y = 2-N (2-pyridinyl), Z = H
4: X = Cl, Y = 4-N (4-pyridinyl), Z = CH_3
5: X = Cl, Y = CH, Z = H

heterocyclic compounds and to clarify their reaction mechanisms.

Only two other synthetic methods for the benzonaphthyridinones have been reported:[9−11] one is an intramolecular amide formation reaction of 2-(*o*-hydroxylaminophenyl)-3-alkoxylcarbonylpyridine, followed by deoxygenation with phosphorus trichloride.[9] The other is an oxidative photocyclization of *N*-(2-pyridinyl)cyclohex-1-enecarboxamide[10] and *N*-pyridinylbenzamide.[11]

There are a few studies on the intramolecular photocyclization mechanism. Grimshaw and de Silva[5b] reported that the photoreaction of 2-chlorobenzanilide afforded a sole product, phenanthridone, although the triplet energy is not high enough for the homolytic cleavage of the C−Cl bond, while the bromo analogue produced a photoreduced product, benzanilide, and thus suggested a type of anchimeric assistance mechanism whereby the phenyl ring can, through its π-cloud, complex the developing radical center in stretching the C−Cl bond and thus lower the transition energy for the reaction. However, the reaction mechanism for the cyclization is not yet clear.

Here, we wish to report the photochemical synthetic method of the benzonaphthyridinones from the photoreaction of 2-halo-*N*-pyridinylbenzamide (**1**−**4** in Chart 1) and its reaction mechanism on the basis of the results of the preparative, kinetic, and laser flash photolysis studies and the known reactivity of 2-chlorobenzanilide (**5** in Chart 1).

Results and Discussion

2-Halo-*N*-pyridinylbenzamides (**1**−**3** in Chart 1) were prepared by reacting 2-halobenzoyl chlorides with the corresponding aminopyridines. To compare the structural effect on the photocyclization, 2-chloro-*N*-methyl-*N*-(4-pyridinyl)benzamide (**4** in Chart 1) was prepared by methylation of **1a**. The preparation details of these haloarene will be described in the Supporting Information.

Preparative Reaction. When a weak basic aqueous acetonitrile solution of 2-chloro-*N*-(4-pyridinyl)benzamide (**1a**, 233 mg, acetonitrile 220 mL, 0.05 N aqueous Na_2CO_3 20 mL) was irradiated with a high-pressure mercury lamp (150 W) for 4 h, a cyclized product, benzo[*c*][1,6]-naphthyridin-6(5*H*)-one (**6**), was obtained in 82% yield (Scheme 1). In pure acetonitrile, the cyclized product **6** was obtained in high yield (86%) but a pyridinium salt was deposited on the outside of the immersion sleeve of the lamp and should be scraped out from time to time during reaction. Thus, a weak basic solution for the photoreaction of other halobenzamides, in which the pyridinium salts were liberated, was used for convenience. The reaction products and their yields in the photoreaction of a series of 2-halo-*N*-pyridinylbenzamide **1**−**4** are summarized in Scheme 1 and Table 1.

Chlorobenzamide **2**a also produced two isomeric cyclized products **7** (21%) and **8** (33%) with minor photo-Fries-type products **12** (9%) and **13** (6%). Chlorobenzamide **3a** exclusively afforded a cyclized product **9** (63%) with small amounts of photo-Fries-type products **14** (3%) and **15** (3%).

2-Chloro-*N*-methyl-*N*-pyridinylbenzamide, which cannot exist as intramolecularly and intermolecularly hydrogen-bonded forms, also produced a photocyclized product, **16** (85%), effectively.

Bromobenzamide **1b** produced a photoreduced product, *N*-(4-pyridinyl)benzamide (**1c**, 37%) with minor photocyclized product. Photoreaction of 2-bromobenzamides **2b** and **3b** also afforded photoreduced products, *N*-(3-pyridinyl)benzamide (**10**) and *N*-(2-pyridinyl)benzamide (**11**), respectively.

In general, *o*-chloro-pyridinylbenzamide **1a**, **2a**, and **3a** underwent intramolecular photocyclization reaction with insignificant photo-Fries type reaction, while *o*-bromo analogues **1b**, **2b**, and **3b** took part in photoreduction reaction with minor photocyclization reaction. The photocyclization propensities of the 2-halopyridinylbenzamides **1**−**3** are similar to that of 2-chlorobenzanilide.[5b] The high yield and simple performance give their photocyclization of 2-chloro analogues preparative valuable for the synthesis of some otherwise difficultly accessible benzo[*c*]naphthyridinones.

Kinetics: Quantum Yield. First of all, the ultraviolet absorption spectral change versus irradiation time was measured upon irradiation of 2-chloro-*N*-(4-pyridinyl)-benzamide (**1a**) in acetonitrile with monochromatic light of wavelength 270 nm (Figure 1). The spectral changes show that photocyclization of **1a** is almost the sole reaction and that the kinetic studies for the photocyclization are possible under several reaction conditions.

The quantum yield of the photocyclization of **1a**, **4**, **5**, **2a**, and **3a** under argon was measured by the UV absorption change at λ_{max} of the cyclized products (at 322 nm for **1a**) and are shown in Table 2. The quantum yields range from a value of 0.52 for **4** to 0.03 for **5**. The photocyclization reactivity of 2-chloropyridinylbenzamide (**1a**, $\Phi = 0.13$) is four times as reactive as 2-chlorobenzanilide (**5**, $\Phi = 0.03$). The reactivity enhancement 2-chloropyridinylbenzamide implies that the role of pyridinyl nitrogen is important in the cyclization and is involved somehow. We assume that phenyl-type σ and chlorine radicals are generated by photoreaction of **1a** and then while chlorine radical is holding the pyridinyl ring by its n-complexation[13] with n-electrons on pyridinyl nitrogen (**17** in Scheme 2), the phenyl σ radical cyclizes to give 2,3-dihydrocyclohexadienyl radical (**18**) and eventually benzo[*c*][1,6]naphthyridinone (**6**).

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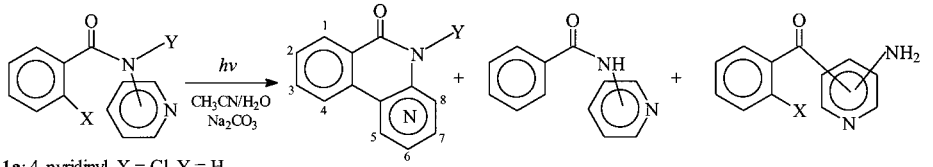
(13) We call n-complex of Cl radical for the complex between chlorine radical and n-electrons on pyridinyl nitrogen.

Scheme 1



1a: 4-pyridinyl, X = Cl, Y = H
2a: 3-pyridinyl, X = Cl, Y = H
3a: 2-pyridinyl, X = Cl, Y = H
1b: 4-pyridinyl, X = Br, Y = H
2b: 3-pyridinyl, X = Br, Y = H
3b: 2-pyridinyl, X = Br, Y = H
4: 4-pyridinyl, X = Cl, Y = CH_3

6: 6-N, Y = H
7: 7-N, Y = H
8: 5-N, Y = H
9: 8-N, Y = H
16: 6-N, Y = CH_3

1c: 4-pyridinyl
10: 3-pyridinyl
11: 2-pyridinyl

12: 3-NH_2, 2-(2-chlorobenzoyl)
13: 3-NH_2, 6-(2-chlorobenzoyl)
14: 2-NH_2, 3-(2-chlorobenzoyl)
15: 2-NH_2, 5-(2-chlorobenzoyl)

Table 1. Products and Their Yields in the Photoreaction of 2-Halo-*N*-pyridinylbenzamide in Basic Aqueous Acetonitrile Solution[a]

reactant	reaction time(h)	isolated product	yield (%)	mp (°C)	lit. mp (°C)
1a	4.0	**6**	82	305.4[b]	303−305[11]
2a	6.0	**7**	21	305.7[b]	
		8	33	299.0[b]	
		12	9	118−119	
		13	6		
3a	5.0	**9**	63	275.1[b]	275−276[11]
		14	3		
		15	3		
1b	2.5	**6**	6	208.0−208.5	
		1c	37		
2b	6.5	**10**	26	113−114	
3b	5.0	**11**	42	80−81	80−83[12a] 82−84[12b]
4	3.0	**16**	85	174−175	

[a] CH_3CN/0.05 N aq Na_2CO_3 = 11/1 (v/v). [b] Measured by digital scanning calorimeter (DSC).

The presence of a similar complex between chlorine radical and pyridine derivatives has been recognized by Breslow and co-workers[14] in explanation of photochemically initiated radical chlorination of 2,3-dimethylbutane and steroid in the presence of pyridine derivatives. This type of complexation is also used in explanation of regioselectivity in the reaction of chlorine atom with quinoline derivative.[15]

Protonation to **1a** lowered the quantum yield (0.05), probably due to a lack of the n-electrons on pyridinyl nitrogen by the protonation. The result supports the assumption.

The quantum yield of photocyclization of **4** is four times as high as that of **1a**. This and preparative results for **4** indicate a conformation intramolecularly hydrogen-bonded between chlorine and hydrogen on amide nitrogen and/or intermolecularly hydrogen-bonded between two amide bonds is not important in the cyclization. Rather, a free or less conjugated conformation from 2-chloro-*N*-methyl-*N*-pyridinylbenzamide effectively produces the cyclized product.

The photocyclization reactivity of **3a** is half as reactive as **1a**, probably because of the orientation factor of the available ortho position of substituted pyridine toward phenyl σ radical formed from the photohomolysis of aryl−Cl bond. The quantum yield of the photocyclization of **2a** is lower than that of **3a**. Presumably, a weak n-complexation of chlorine radical with 3-pyridinyl nitrogen because of a lack of electron donation by resonance of amide nitrogen, slows down the intramolecular arylation and in turn a photo-Fries-type reaction can compete with the cyclization reaction.

In the presence of oxygen, the quantum yield of the photocyclization of **1a** lowered by one-third and those of **2a** and **3a** also lowered by about one-half (inset, Figure 1 and Table 3). These observations imply that triplet states are involved in the photocyclization of **1a**, **2a**, and **3a**. This conclusion was confirmed by sensitizing the reaction of **1a** with acetone or acetophenone as sensitizer: irradiation of an acetonitrile solution of **1a** with acetone (or acetophenone) at monochromatic light of wavelength 325 ± 10 nm (or 325 ± 10 nm for acetophenone), in which acetone (or acetophenone) only absorbed, produced **6** efficiently (vide infra).

Stern−Volmer plot of the photocyclization of **1a** with a triplet quencher, isoprene, has been performed (Supporting Information). The plot of Φ_o/Φ versus isoprene concentration gave a straight line with an intercept of unity, indicating a triplet state involved in the reaction. The $K_Q\tau$ value was 194 M^{-1}. If K_Q is assumed as the diffusion-controlled rate in water ($K_Q = 6.4 \times 10^9$ M^{-1} s^{-1}),[16] the lifetime of the triplet state of **1a** is 30 ns (lower limit).

It is noteworthy that the photoreduction of **1b** did not occur in the presence of oxygen: the reduced product, *N*-(4-pyridinyl)benzamide (**1c**), was not seen in the presence of oxygen in GC [the peak of the cyclized product was disturbed by that of the starting material, lower GC/NPD (nitrogen and phosphorus sensitive detector), not shown]. The reduction was also sensitized by acetophenone in the absence of oxygen (not shown). Thus, the reduction is also a triplet-mediated reaction.

Kinetics: Relative Rate. To decide the cyclization mechanism, the relative reaction rates of **1a** were investigated in several conditions and are shown in Table 4. In the presence of water and aqueous base, the cyclization of **1a** was retarded, but a photoreduction was accelerated slightly (entries 1−5 in Table 4). Probably, the retardation is attributed to the lack of the availability of n-electrons of pyridinyl group because of hydration.

The trace amount of **1c** observed in the preparative photoreaction of **1a** and the formation of **1c** measured in the kinetic studies, albeit at a low rate, are meaningful, because they indicate the other route of phenyl-type σ radical to the reduction.

In the presence of a strong base such as NaOH, the photocyclization reactivity lowered by one-fifth while the photoreduction accelerated (entry 5 in Table 4). In fact

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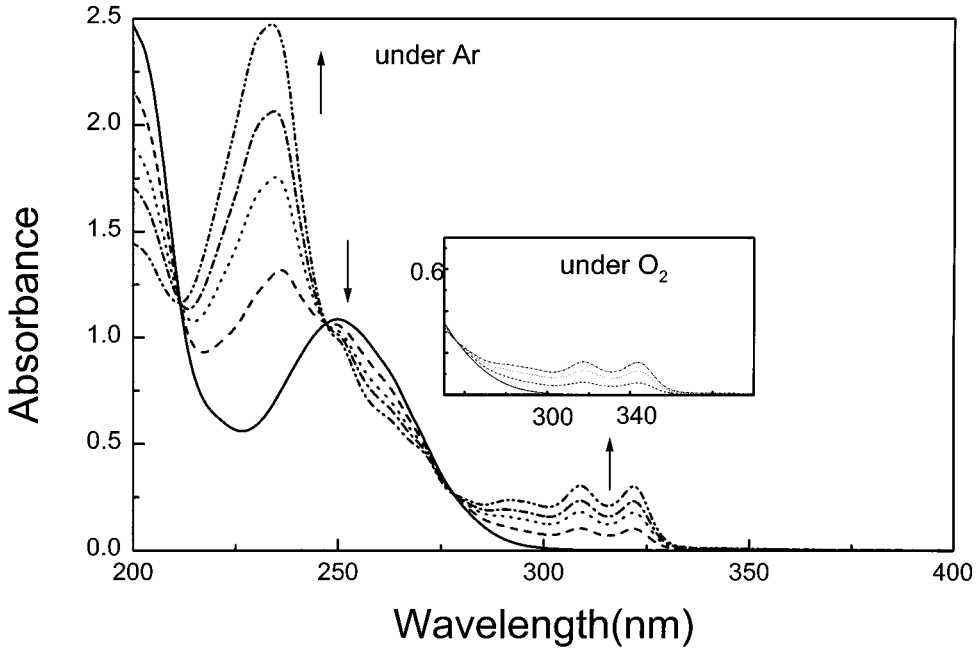


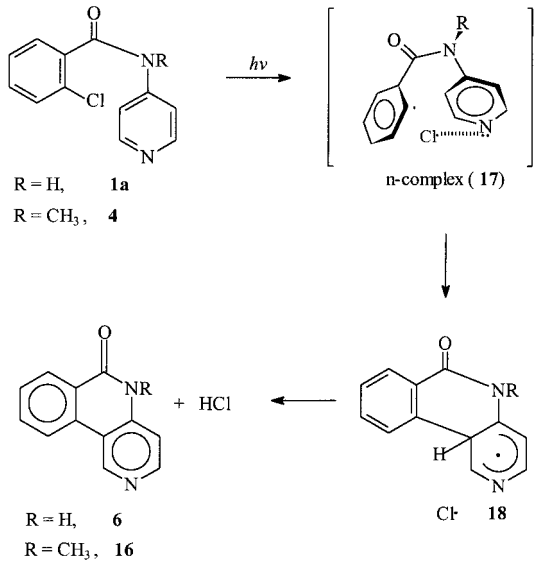
Figure 1. Spectral change during the photoreaction of **1a** in deaerated solution (Ar) and in aerated solution (O_2, inset). Irradiation time for the deaerated solution: —, 0 min; — — —, 7.5 min; - - -, 15 min; - • -, 22.5 min; - •• -, 37.5 min. Irradiation time for the aerated solution (inset): —, 0 min; — — —, 15 min; - - -, 30 min; - • -, 45 min.

Table 2. Quantum Yield for the Intramolecular Photocyclization of 2-Chloro-*N*-pyridinylbenzamides and 2-Chlorobenzanilide (1a, 4, and 5) in Acetonitrile under Argon

reactant	product	Φ	ratio (Φ_x/Φ_{1a})
1a	**6**	0.13	1.0
1a protonated[a]	**6**	0.05	0.4
4	**16**	0.52	4.0
5	phenthridone	0.03	0.2
2a	**7** + **8**[b]	0.04	0.3
3a	**9**	0.07	0.5

[a] In the presence of *p*-toluenesulfonic acid (1 equiv). [b] The molar absorptivity of **7**and **8** at 340 nm are assumed to be the same (ϵ = 9.7×10^3 L/mol·cm).

Scheme 2



the UV absorption spectra of **1a** changed in the presence of a strong base such as NaOH: the λ_{max} (247.0 nm) of **1a** in acetonitrile was shifted to 294 nm in 1 M NaOH (2%, v/v) acetonitrile, indicating the presence of an imidol

Table 3. Quantum Yield on the Intramolecular Photocyclization of 2-Halo-*N*-pyridinylbenzamide (1a, 2a, and 3a) with and without Oxygen

		quantum yield (Φ)		
reactant[a]	product	with Ar	with O_2	ratio (Φ_{Ar}/Φ_{O2})
1a	**6**	0.13	0.04	3.2
2a	**7** + **8**[b]	0.03	0.02	1.5
3a	**9**	0.07	0.03	2.3

[a] Measured with 2.0×10^{-4} M reactant in 0.3% basic aqueous acetonitrile solution (2.0×10^{-4} M NaOH). [b] The molar absorptivity of **7** and **8** at 340 nm are assumed to be the same ($\epsilon = 9.7 \times 10^3$ L/mol·cm).

Table 4. Relative Rate of the Formation of the Cyclized and Reduced Products (6 and 1c) in the Photoreaction of 2-Chloro-*N*-(4-pyridinyl)benzamide (1a) under Nitrogen Atmosphere in Several Conditions

		relative rate	
entry	solvent	reduced reaction (**1c**)	cyclized reaction (**6**)
1	CH_3CN[a]	t[c]	1.0
2	CH_3CN/H_2O (9/1)	t[c]	0.8
3	CH_3CN/H_2O (9/1) 0.5 mM Na_2CO_3	0.1	0.7
4	CH_3CN/H_2O (9/1) 1.5 mM Na_2CO_3	0.1	0.5
5	CH_3CN/H_2O (9/1) 2 mM NaOH	0.2	0.2
6	CH_3OH	t[c]	0.2
7	CH_3CN 3 mM MMA[b]	t[c]	0.8

[a] Treatment NaOH after the reaction for liberation of pyridinium salt. [b] Methyl methacrylate. [c] Trace, less than 0.03.

configuration. The excited state of the imidol,[8] which is probably a charge-transfer species and is different from the excited state of **1a** in acetonitrile, is attributed to the lower cyclization reactivity in a strong base. In methanol the cyclization reaction was retarded by one-fifth. The low reactivity of **1a** in methanol can be explained by lowering the availability of n-electrons of the pyridine ring for a species which holds the pyridine ring for the

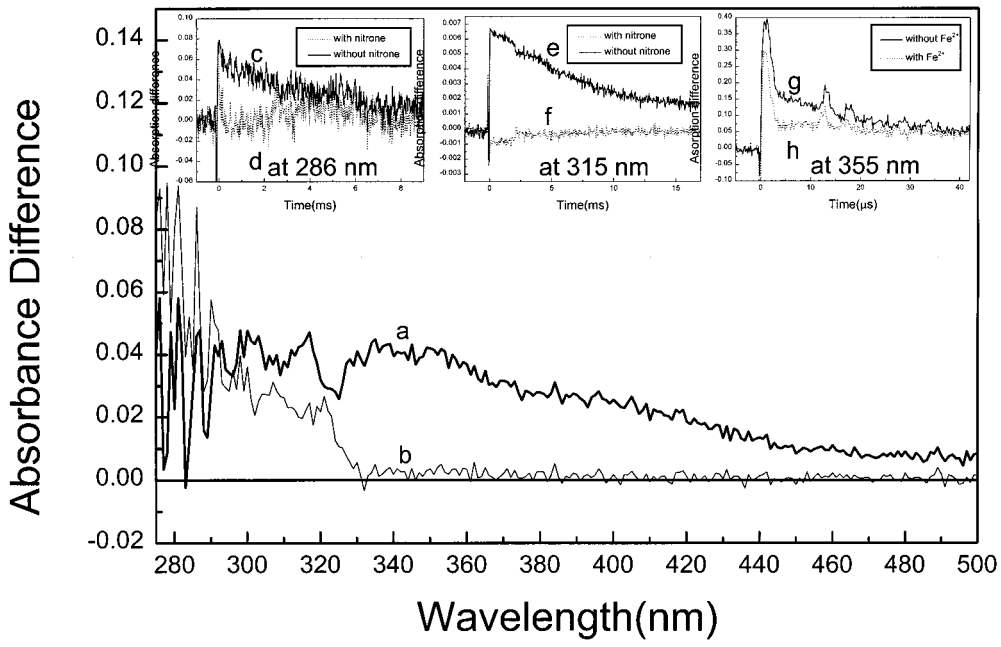


Figure 2. Transient absorption spectra: curve a (thick solid line), measured 10 μs after the laser pulse for **1a** (1.7×10^{-4} M) in acetonitrile containing tetramethylammonium chloride (5.9×10^{-4} M) under argon; curve b (thin solid line), measured 1 ms after the laser pulse for the same solution. The c and d curves in the left inset are the temporal profile of 286 nm transient and the same curve in the presence of *N*-*tert*-butyl-α-phenylnitrone, respectively. The e and f curves in the middle inset are the temporal profile of 315 nm transient and the same curve in the presence of *N*-*tert*-butyl-α-phenylnitrone, respectively. The g and h curves are the temporal profile of 355 nm transient and the same curve in the presence of potassium hexacyanoferrate(II), respectively.

cyclization (entry 6). In the presence of a radical scavenger MMA (methyl methacrylate), the cyclization was retarded (entry 7), again indicating a radical reaction involved.

Laser Flash Photolysis. Transient absorption spectra were obtained from the laser flash photolysis of 2-chloro-*N*-(4-pyridinyl)benzamide (**1a**) in argon-saturated acetonitrile containing tetramethylammonium chloride, as shown in Figure 2. The overall transient absorption spectrum at 10 μs delay after laser flash (thick solid line, curve a in Figure 2) exhibited a broad spectral feature in the entire probe wavelength region with two rather broad absorption peaks in 300−320 nm and 330−360 nm region and one weak and diffuse peak in 390−440 nm region. At 1 ms delay after the flash, the absorption increase in the shorter wavelength region became manifest as compared with that at 10 μs delay. In addition, the absorption band in 300−320 nm lost its intensity, and the bands in 330−360 nm and 390−440 nm region completely disappeared (thin solid line, curve b in Figure 2).

In this broad absorption spectra, the transient absorption at about 355 nm is believed to be due to dichloride radical anion, $Cl_2^{\bullet-}$, the lifetime of which is 15 μs in acetonitrile (curve g in right inset, Figure 2), because the transient absorption was suppressed by addition of potassium hexacyanoferrate(II) (curve h in right inset, Figure 2).[17] The fact that the transient absorption of dichloride radical anion is formed when chlorine radical is generated in the presence of chloride anion, is well-known.[18] It is noteworthy that the transient is seen in the laser flash photolysis of **1a** even in the absence of tetramethylammonium chloride although the band is weak. It is also noteworthy that the transient species is not seen at the outset of the photolysis, but is seen at the latter stage of the reaction with digital oscilloscope. This implies that the dichloride radical anion is not formed unless HCl is produced in the photocyclization. Since the dichloride radical anion is detected, counterpartner, a phenyl σ radical should be observed.

The transient intermediate observed at about 286 nm at 1 ms delay is assignable to phenyl σ produced by the photohomolysis of the aryl−chlorine bond of **1a**, because the absorption region is the same as a phenyl σ radical from *N*-(2-chlorobenzyl)pyridinium salt,[7] and the species is not seen in the laser photolysis of **1c** (not shown). The temporal profile of the transient species at 286 nm from **1a** is shown in the left inset of Figure 2. The transient species decays in a first-order process and its lifetime is 5.9 ms. As expected, the species is suppressed by the addition of a radical scavenger, *N*-*tert*-butyl-α-phenylnitrone (curve d in the left inset).

The transient species observed in 300−320 nm region exhibits a single-exponential decay with a lifetime of 1.8 ms and a significant reduction in the presence of a radical scavenger, *N*-*tert*-butyl-α-phenylnitrone (middle inset, Figure 2). Thus, the transient species in this region is assignable to a conjugated 2,3-dihydropyridinyl radical. The diffuse transient species observed from 390 to 440 nm from photolysis of **1a** is assigned to n-complex of Cl radical with n-electron pair of pyridine moiety of **1a** (Scheme 2).

The assignment was confirmed by the following competition experiment. The effects of tetramethylammonium chloride (TMAC) and pyridine on the transient at 400 nm from the laser flash photolysis of **1a** in acetoni-

(17) Anbar, M.; Thomas, J. K. *J. Phys. Chem.* **1964**, *68*, 3829.

(18) (a) Scaiano, J. C.; Barra, M.; Calabrese, G.; Siuta, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1418. (b) Jayson, G. G.; Parson, B. J.; Swallow, A. J. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1597. (c) Grossweiner, L. I.; Matheson, M. S. *J. Phys. Chem.* **1957**, *61*, 1089.

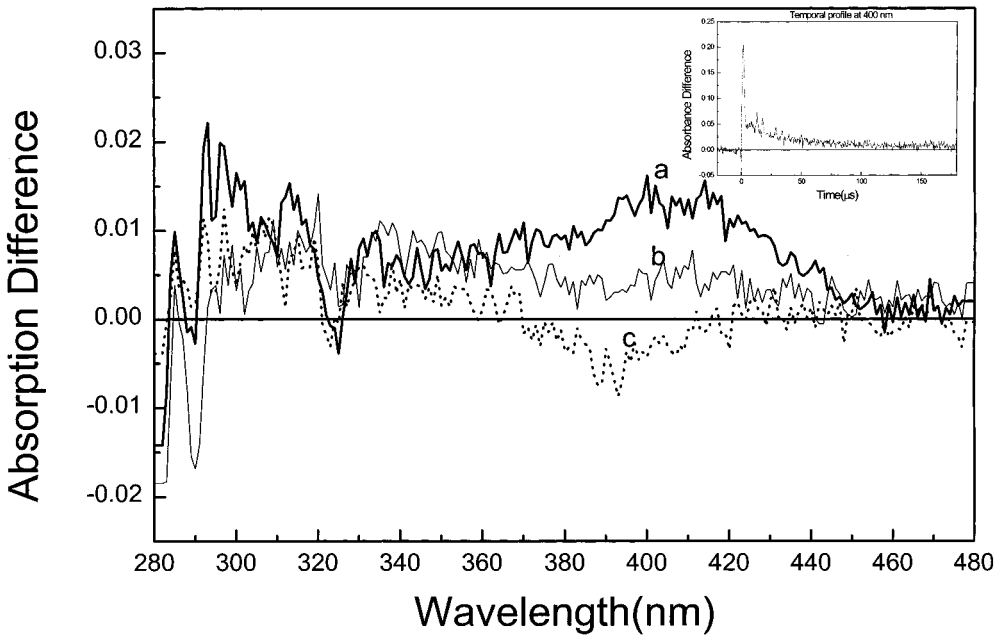
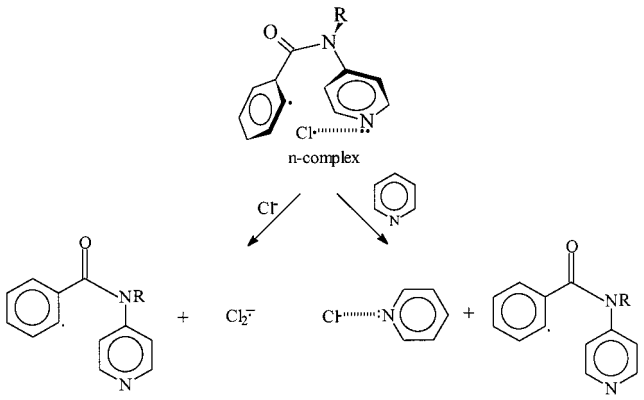


Figure 3. Transient absorption spectra: curve a (thick solid line), measured 5 μs after the laser pulse (266 nm) for **1a** (1.2×10^{-4} M) in acetonitrile under argon; curve b (thin solid line), measured 5 μs after laser pulse for the same solution with TMAC (1.2×10^{-4} M); curve c (dot line), measured 5 μs after laser pulse for the same solution with pyridine (1.2×10^{-4} M). The curve in the right inset are the temporal profile of 400 nm transient from **1a** in acetonitrile.

Scheme 3



trile was carried out and is shown in Figure 3: the thick solid line was obtained 5 μs after laser pulse (266 nm) for **1a** (1.2×10^{-4} M) in acetonitrile under argon; the thin solid and dot lines were obtained 5 μs after laser pulse for the above solution in the presence of TMAC (1.2×10^{-4} M) and pyridine (1.2×10^{-4} M), respectively. The presence of TMAC increased the formation of the $Cl_2^{\bullet-}$ at about 350 nm with expenditure of a transient absorption at about 400 nm. Presumably, a competition reaction of chloride anion (Cl^-) from TMAC for chlorine radical to give dichloride anion radical with pyridinyl moiety of **1a** exists (Scheme 3). In the presence of pyridine both peaks at about 350 and 400 nm decreased. Pyridine competes for chlorine radical with lone pair electron of pyridinyl nitrogen of **1a**.

To confirm the assignment of the n-complex of chlorine in the photoreaction of **1a**, another experiment has been carried out. When a pyridine solution of chlorine was irradiated with pulse laser light (355 nm), two transient absorption spectra were obtained 5 μs and 100 μs after the laser pulse (Figure 4). The absorption at about 390 nm 5 μs after the laser pulse disappeared at 100 μs delay. The lifetime of the 390 nm transient was 65 μs (inset of Figure 4). The absorption position and lifetime of the 390 nm transient are similar to 400 nm-transient from **1a**. Thus, the 400 nm transient from **1a** is assigned to the n-complex of chlorine radical.

The physical properties of the identified transients from the photolysis of **1a** and chlorine in pyridine are summarized in Table 5. The detection of $Cl_2^{\bullet-}$, a phenyl σ, a conjugated-2,3-dihydropyridinyl radicals, and n-complex of chlorine radical suggests a radical-mediated mechanism in the photocyclization.

Energetics. Interestingly enough, the UV absoption maxima of 2-chloro-*N*-(4-pyridinyl)benzamide (**1a,** λ_{max} 247 nm, $\epsilon = 1.5 \times 10^4$ L/mol·cm) and 2-bromo-*N*-(4-pyridinyl)benzamide (**1b**, λ_{max} 247 nm, $\epsilon = 1.7 \times 10^4$ L/mol·cm) in acetonitrile are shorter than that of unsubstituted *N*-(4-pyridinyl)benzamide (**1c**, λ_{max} 259 nm, $\epsilon = 1.7 \times 10^4$ L/mol·cm), suggesting that the conformation of **1a** and **1b** are less conjugated. In other words, 2-halobenzamide **1a** and **1b** adopt conformations which are rather nonconjugated or distorted due to the nonbonded ortho interaction (Chart 2). The distorted conformers of **1a** and **1b** weaken the bond strength of the aryl−X bond for the photohomolytic cleavage. Furthermore, it is assumed that the less conjugated conformer of the ground-state results in a localized excited state of the 2-halopyridinylbenzamide and rises the energy level.

The excitation and fluorescence spectra of **1a** in acetonitrile are shown in the Supporting Information. The resulting structured absorption and emission spectra are mirror images, indicating the excited-state structure is not different from that of the ground state. The spectra show that the energy of the singlet excited state of **1a** is 89 kcal/mol.

The phosphorescence measurement of **1a** showed that the onset energy of the triplet state is 78 kcal/mol. The photocyclization of **1a** is readily sensitized by triplet sensitizers such as acetone and acetophenone (Table 6). However, the reaction with a triplet sensitizer, benzophe-

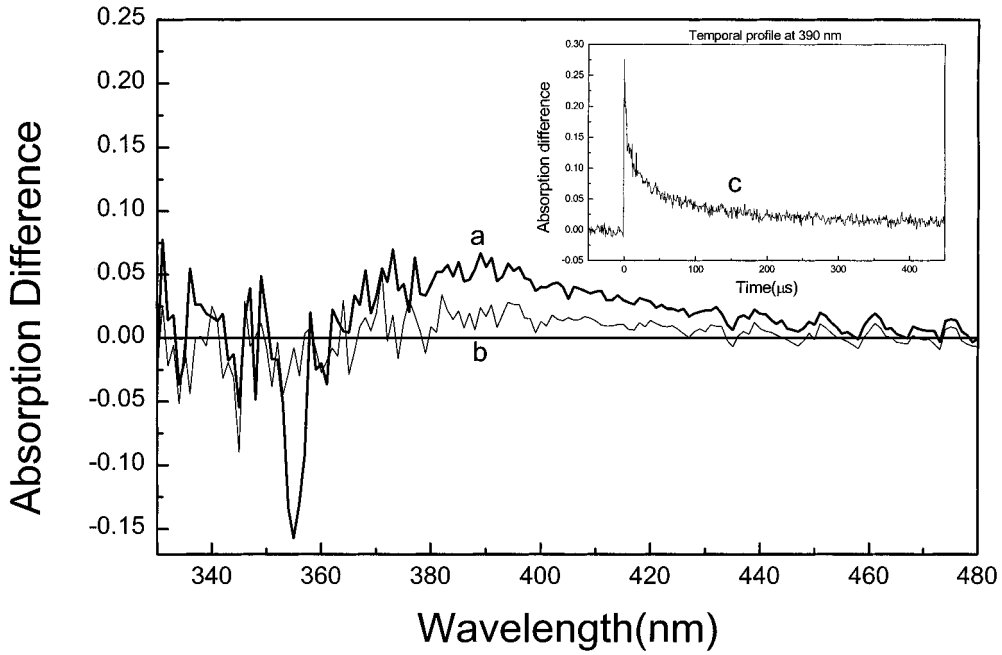
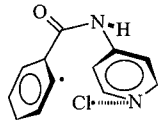
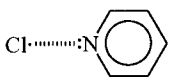
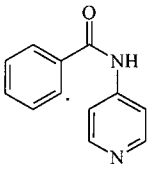
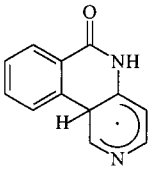


Figure 4. Transient absorption spectra: curve a (thick solid line), measured 5 μs after laser pulse (355 nm) of chlorine in pyridine under argon; curve b (thin solid line), measured 100 μs after laser pulse for the same solution. The c curve in the right inset are the temporal profile of 390 nm transient.

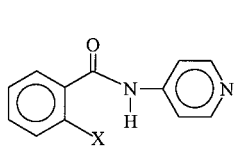
Table 5. Physical Properties of the Transient Intermediates from the Photolysis of 1a

transient	λ_{max} nm	lifetime	remark (reactant)
	400	30μs	laser 266 nm (**1a**)
	390	65 μs	laser 355 nm (Cl_2 and pyridine)
	286	5.9 ms	laser 266 nm (**1a**)
 **18**	315	1.8 ms	laser 266 nm (**1a**)
Cl_2^-	355	15 μs	laser 266 nm (**1a**)

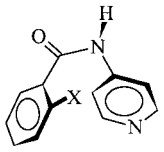
none, occurred ineffectively. The sensitization reactivity is understandable by comparing the triplet energy[19] of the sensitizer with that of **1a**: the triplet energy of benzophenone (69 kcal/mol) is lower than that of **1a** (78 kcal/mol). The triplet energy of acetone (78 kcal/mol) is high enough to induce a triplet state of **1a** to undergo the cyclization effectively, but that of acetophenone (74 kcal/mol) is a little lower than or comparable to that of **1a** at room temperature. It is noteworthy that the sensitizing cyclization of **1a** with acetophenone at 10 °C was three times efficient as compared with that at 0 °C. This shows that the population of the appropriate triplet state for the homolysis is increased at higher temperature.

The only problem in this interpretation is that the bond energy of aryl−chlorine should be lower than the triplet

Chart 2



conjugated conformer



distorted and less conjugated conformer

1a X = Cl
1b X = Br
1c X = H

Table 6. Relative Rate on the Sensitized Photocyclization of 1a at 20 °C[a]

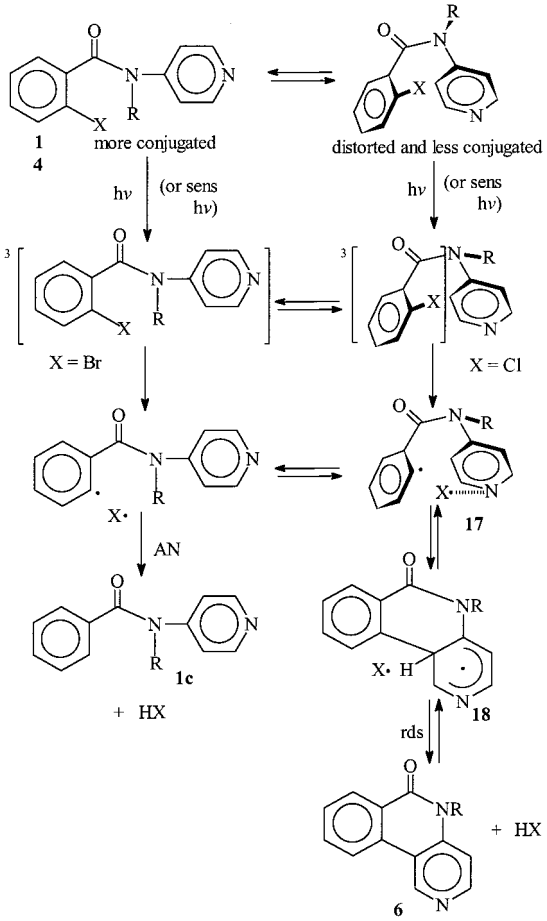
sensitizer	E_T[19] (kcal/mol)	relative rate
acetone	78	10
acetophenone	74	1.0
benzophenone	69	0.3
no sensitizer		0.1

[a] Irradiation wavelength, 325 ± 10 nm.

energy of **1a** (78 kcal/mol) or at least comparable to it. According to previous reports,[20,21] the bond energy of aryl−chlorine is quite lowered in *o*-substituted chlorobenzene: that of *o*-dichlorobenzene is 86 kcal/mol. The aryl-chlorine bond energy is 81 kcal/mol in 2-chlorobenzoic acid. Assuming that the bond energy of aryl−chlorine of **1a** is about 81 kcal/mol, the homolytic cleavage of aryl−chlorine bond is possible from the triplet state of **1a** (78 kcal/mol) at room temperature.

Mechanism. The following photocyclization mechanism is proposed on the basis of the above preparative, kinetic, and laser flash photolysis studies (Scheme 4). Upon irradiation, the distored and less conjugated conformer of o-substituted pyridinylbenzamide is excited to populate the singlet state and the ensuing intersystem crossing populates the triplet state. The triplet states can also be populated by the energy transfer of a sensitizer such as acetone or acetophenone. The majority of the triplet energy is assumed to reside at the 2-chlorobenzoyl moiety, not the aminopyridinyl moiety because of the nonconjugated system. The triplet state of the 2-chlorobenzoyl moiety of **1a** undergoes homolytic cleavage of the phenyl−chlorine bond to yield a phenyl σ radical and chlorine radical, while the triplet state of the more conjugated conformer of **1a** does not experience homolytic cleavage of the phenyl−chloride bond due to the lower triplet energy of the conjugated conformer. The chlorine radical interacts with the lone pair electrons on pyridinyl nitrogen to give n-complex of chlorine radical, or/and reacts with chloride anion to yield dichloride radical anion, if chloride anion is formed. The photogenerated phenyl σ radical now partitions between reacting with the neighbor pyridine ring to form conjugated 2,3-dihydropyridinyl radical while chlorine radical holds the pyridinyl ring by the n-complexation of chlorine radical (**17**) and the ensuing dehydrogenation of the conjugated radical eventually proceeds to give benzo[*c*]naphthyridinone product (**6**), and reacting with hydrogen donor to form the reduced product (**1c**). Observation of a small amount of a photoreduced product from **1a**, **2a**, or **3a** in preparative scale with GC/MS[22] and in the relative rate study of **1a** is in line with the radical-mediated mechanism.

Scheme 4



For 2-bromo-*N*-pyridinylbenzamide (**1b**, **2b**, **3b**), photoreduction reactions occur because bromine radical, which is produced from the photohomolytic cleavage of phenyl−bromine bond, cannot hold the pyridinyl ring due to the lack of the n-complexation of bromine radical. A similar behavior of bromine radical was observed in regioselectivity of quinoline derivatives.[15] The triplet energy of the more conjugated conformer which is lower than that of the distorted and less conjugated one can split only the aryl−bromine bond (not the aryl−chlorine bond) to give a phenyl-type σ and bromine radicals. The phenyl-type σ radical is mainly reduced by hydrogen abstraction from the environment with the minor cyclized product.

The photocyclization mechanism in which n-complex is involved can be applied in ring formation. For example, photoreaction of 2-chloroarene tethered to arene containing nitrogen can afford cyclized products.

The photocyclization mechanism suggests that in the photocyclization of 2-chlorobenzanilide a π-complex of the photogenerated chlorine radical with the phenyl ring is involved. Further application of these mechanisms, in which n- and π-complexes of chlorine radical are involved,

(19) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993; p 4.
(20) Cioslowski, J.; Liu, G.; Moncrieff, D. *J. Phys. Chem. A.* **1997**, *101*, 957.
(21) Sabbah, R.; Agulia, A. R. *Can. J. Chem.* **1995**, *73*, 1538.

(22) In the preparative scale, the reduced products were not separated, although the products were identified and quantitatively measured by GC/MS (less than 3%).

to other molecular systems and 2-chlorobenzanilides will be described in due course.

Experimental Section

Material and General Procedures. 2-Chlorobenzoyl chloride, 2-bromobenzoyl chloride, 4-aminopyridine, 3-aminopyridine, and 2-aminopyridine (all Aldrich) were used without further purification. Triethylamine (Aldrich) and methyl methacrylate (Aldrich) were distilled prior to use. Acetonitrile and methanol were distilled prior to use. Sodium carbonate and sodium hydroxide (reagent grade) were used without purification. Acetophenone (Fluka) and benzophenone (Fisher) were used as received. Triply distilled water was used.

Melting points were measured on capillary melting point apparatus, Thomas-Hoover or digital scanning calorimeter (DSC). Uv/vis absorption spectra were recorded on Varian Cary 3E Spectrophotometer or Hewlett-Packard 8452A diode array spectrophotometer. Perkin-Elmer LS-50 luminescence spectrophotometer with a gated photomultiplier tube detector at 77K with modification of cell compartment was used for the phosphorescence spectra. For the fluorescence spectra, Spectrofluorimeter (Spex, Model FL 111) was used. Infrared spectra were recorded on Nicolet Magna 550 FT-IR (Mattson Galax Series 7020) spectrophotometer or Hewlett-Packard IRD equipped 5890 Series II gas chromatograph. Gas chromatograph with NPD (6890 Series Hewlett-Packard) was used. NMR spectra were recorded on Brucker Ac 200 (200 MHz) operating at 200 MHz for proton. The ^{1}H NMR spectra were referenced with respect to TMS. The mass spectra were obtained from Hewlett-Packard 5989A mass spectometer with Hewlett-Packard 5890 series II gas chromatograph. Elemental analysis was performed on elemental analyzer, Carlo Erba CHNS-O E. A. 1180.

Preparative Photoreaction. Photoreaction of 2-Chloro-*N*-(4-pyridinyl)benzamide (1a): General Procedure. To a large (300 mL) quartz immersion well photolysis unit with provision for circulation nitrogen was added 220 mL of an approximately 4.2×10^{-3} M acetonitrile solution of 2-chloro-*N*-(4-pyridinyl)benzamide (**1a**, **2a**, **3a**, **1b**, **2b**, or **3b**) containing 20 mL of 0.05 N Na_2CO_3 aqueous solution. With nitrogen circulation, the solution was irradiated with a 150 W mercury lamp (high pressure) at 100 V for 4 h (The proceeding of the reaction was followed by TLC or GC). After stripping off solvent under reduced pressure, recrystallization ($EtOH/H_2O$ = 8.5/1.5) gave benzo[*c*][1,6]naphthyridin-6(5*H*)-one (**6**, 82%): mp (DSC) 305.7 °C (lit.[11] mp 303−304.5 °C); UV (λ_{max} in acetonitrile) 322 nm ($\epsilon = 6.6 \times 10^3$ L/mol·cm); IR (gas phase) 3430, 3079, 1715 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 11.92 (br s, 1H), 9.55 (s, 1H), 8.62 (d, J = 7.9 Hz, 1H), 8.48 (d, J = 5.6 Hz, 1H), 8.31 (dd, J = 7.9, 1.1 Hz, 1H), 7.87 (dt, J = 1.4, 7.6 Hz, 1H), 7.67 (dt, J = 1.0, 7.6 Hz, 1H), 7.25 (dd, J = 5.6, 0.5 Hz, 1H); MS (EI) *m*/*z* (rel intensity) 196 (100, M$^+$), 168 (22). Anal. Calcd for $C_{12}H_8ON_2$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.42; H, 3.91; N, 14.30.

Photoreaction of 2-Bromo-*N*-(4-pyridinyl)benzamide (1b). The photoreaction of **1b** was carried out for 2.5 h as in the case of **1a**. The photolysate of **1b** was evaporated under reduced pressure. The dissolved portion of the photolysate in acetonitrile was separated in a column chromatograph with a solvent mixture [$CH_3CN/CH_2Cl_2/EtOH$ = 6/18/1, (v/v)]. The band of R_f 0.39 on TLC was identified as benzo[*c*][1,6]-naphthyridin-6(5*H*)-one (6%). The band of R_f 0.45 was identified *N*-(4-pyridinyl)benzamide (**1c**, 37%; mp, 208.0−208.5 °C).

Photoreaction of 2-Chloro-*N*-(3-pyridinyl)benzamide (2a). The photoreaction of **2a** (233 mg, 1 mmol) was carried out for 6 h as in the case of **1a**. After the solvent was stripped off, the photolysate was dissolved three times in diethyl ether (5 mL × 3) and the solid was separated from the mixture by a centrifuge. After the solids were dissolved with methanolic triethylamine (triethylamine (0.2 mL) and methanol (3 mL)) the solution again was evaporated to 1 mL. Analytical TLC showed two bands of R_f 0.24 and 0.57. The bands were separated by column chromatograph with an eluent of $CH_3CN/CH_2Cl_2/EtOH$ = 6/18/1 (2.2 × 24 cm, 70−230 mesh silica gel). The band of R_f 0.24 was identified as benzo[*c*][1,7]-naphthyridin-6(5*H*)-one (**7**, 41 mg, 21%): mp (DSC) 305.7 °C; UV (λ_{max} in acetonitrile), 336 nm ($\epsilon = 5.5 \times 10^3$ L/mol·cm); IR (gas phase) 3429, 3080, 1712 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 11.90 (br. s, 1H), 8.67 (s, 1H), 8.60 (d, J = 8.2 Hz, 1H), 8.42−8.29 (m, 3H), 7.93 (dt, J = 1.5, 7.6 Hz, 1H), 7.78 (t, J = 7.5 Hz, 1H); MS (EI) *m*/*z* (rel intensity) 196 (100, M$^+$). Anal. Calcd for $C_{12}H_8ON_2$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.43; H, 3.25; N, 14.09. The band of R_f = 0.57 was identified as benzo[*c*][1,5]naphthyridin-6(5*H*)-one (**8**, 65 mg, 34%): mp (DSC) 299 °C; UV (λ_{max} in acetonitrile), 340 nm ($\epsilon = 1.4 \times 10^4$ L/mol·cm); IR (gas phase) 3428, 3083, 1711 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 11.77 (br. s, 1H), 8.75 (dd, J = 8.2, 0.6 Hz, 1H), 8.53 (dd, J = 4.5, 1.3 Hz, 1H), 8.30 (dd, J = 8.2, 1.3 Hz, 1H), 7.92 (dt, J = 1.4, 7.6 Hz, 1H), 7.79−7.69 (m, 2H), 7.52 (dd, J = 8.2, 4.5 Hz, 1H); MS (EI) *m*/*z* (rel intensity) 196 (100, M$^+$), 168 (27). Anal. Calcd for $C_{12}H_8ON_2$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.54; H, 3.44; N, 14.01. The diethyl ether portion was also separated by HPLC (low-pressure liquid chromatography, silica gel 230−400 mesh, ϕ 2.2 cm × 24 cm) with the following order of eluents, CH_2Cl_2 200 mL, CH_2Cl_2/CH_3CN = 50 mL/350 mL, CH_3CN/CH_2Cl_2 = 100 mL/250 mL, and CH_3CN 300 mL. The analysis gave photo-Fries type products, 3-amino-2-(2-chlorobenzoyl)pyridine (**12**, 21.8 mg, 9%) and 3-amino-6-(2-chlorobenzoyl)pyridine (**13**, 15 mg, 6%, syrup). 3-Amino-2-(2-chlorobenzoyl)pyridine (**12**) was identified by the following spectral data and elemental analysis: mp 118−119 °C; IR (gas phase) 3511, 3370, 3064, 1669 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.98 (dd, J = 4.1, 1.4 Hz 1H), 7.43−7.31 (m, 4H), 7.19 (dd, J = 8.5, 4.1 Hz, 1H), 7.07 (dd, J = 8.5, 1.4 Hz, 1H), 6.27 (br s, 2H); MS (EI) *m*/*z* (rel intensity) 232 (2, M$^+$), 198 (13), 197 (100). Anal. Calcd for $C_{12}H_9ON_2$: C, 61.95; H, 3.90; N, 12.04. Found: C, 61.93; H, 3.94; N, 11.71. 3-Amino-6-(2-chlorobenzoyl)pyridine (**13**) was identified by the following spectral data and elemental analysis: IR (gas phase) 3503, 3419, 3071, 1692 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.04 (d, J = 2.8 Hz 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.44−7.34 (m, 4H), 7.01 (dd, J = 8.5, 2.8 Hz, 1H), 4.32 (br s, 2H); MS (EI) *m*/*z* (rel intensity) 232 (1, M$^+$), 198 (13), 197 (100). Anal. Calcd for $C_{12}H_9ON_2$: C, 61.95; H, 3.90; N, 12.04. Found: C, 61.90; H, 3.95; N, 11.97.

Photoreaction of 2-Bromo-*N*-(3-pyridinyl)benzamide (2b). The photoreaction of **2b** (556 mg, 2 mmol) was carried out for 6.5 h as described above for that of **1a**. GC/MS analysis showed that there were three products, namely photoreduced product (major), photocyclized product, and photo-Fries-type product. Only, the photoreduced product (103.8 mg, 26%) was separated on column chromatography with eluent of $CH_3CN/CHCl_3$ (ϕ 2.2 cm × 25 cm, 70−230 mesh silica gel): mp 113−114 °C; UV (λ_{max} in acetonitrile) 259 nm; IR (gas phase) 3460, 3073, 1710 cm^{-1};^{1}H NMR (200 MHz, acetone-d_6) δ 9.71 (br. s, 1H), 8.97 (d, J = 2.0 Hz 1H), 8.34−8.28 (m, 2H), 8.05−7.99 (m, 2H), 7.63−7.47 (m, 3H), 7.35 (dd, J = 8.0, 4.8 Hz, 1H); MS (EI) *m*/*z* (rel intensity) 198 (24, M$^+$), 105 (100). Anal. Calcd for $C_{12}H_{10}ON_2$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.45; H, 4.96; N, 14.27.

Photoreaction of 2-Chloro-*N*-(2-pyridinyl)benzamide (3a). The photoreaction of **3a** (233 mg, 1 mmol) was carried out for 5 h as described above for that of **1a**. After evaporation of solvent, recrystallization ($EtOH/H_2O$ = 2/1) gave a photocyclized product, benzo[*c*][1,8]naphthyridin-6(5*H*)-one (**9**, 123 mg, 63%): mp (DSC) 275.1 °C (lit.[11] mp 275−276 °C); UV (λ_{max} in acetonitrile) 334 nm ($\epsilon = 1.2 \times 10^4$ L/mol·cm); IR (gas phase) 3426, 3078, 1712 cm^{-1}; ^{1}H NMR (200 MHz, DMSO-d_6) δ 11.97 (br s, 1H), 8.79 (d, J = 8.0 Hz, 1H), 8.54−8.47 (m, 2H), 8.32 (d, J = 7.8 Hz, 1H), 7.88 (t, J = 7.6 Hz, 1H), 7.68 (t, J = 7.54 Hz, 1H), 7.32 (dd, J = 8.0, 4.7 Hz, 1H); MS (EI) *m*/*z* (rel intensity) 196 (100, M$^+$). Anal. Calcd for $C_{12}H_8ON_2$: C, 73.46; H, 4.11; N, 14.28. Found: C, 73.14; H, 3.86; N, 14.18. The filtrate was concentrated and then separated on column chromatography (ϕ 2.2 cm × 25 cm, 70−230 mesh silica gel) with eluent of CH_3CN/CH_2Cl_2 (1/2). Two bands (R_f 0.60, 75 mg and R_f 0.80, 7.5 mg) were obtained and identified as 2-amino-3-(2-chlorobenzoyl)pyridine (**14**) and 2-amino-5-(2-

chlorobenzoyl)pyridine (**15**), respectively by the following data. 2-Amino-3-(2-chlorobenzoyl)pyridine (**14**): mp 156−157 °C; IR (gas phase) 3521, 3377, 3077, 1661 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.26 (dd, J = 4.7, 1.8 Hz, 1H), 7.50−7.28 (m, 5H), 7.06 (br. s, 2H), 6.56 (dd, J = 7.9, 4.7 Hz, 1H); MS (EI) m/z (rel intensity) 234 (6, $M^+ + 2$), 232 (19, M^+), 198 (14), 197 (100). Anal. Calcd for $C_{12}H_8ON_2$: C, 61.95; H, 3.90; N, 12.04. Found: C, 62.16; H, 3.73; N, 11.87. 2-Amino-5-(2-chlorobenzoyl)-pyridine (**15**): mp 133.0−133.5 °C; IR (gas phase) 3520, 3421, 3074, 1681 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 8.38 (d, J = 2.3 Hz, 1H), 7.97 (dd, J = 8.7, 2.3 Hz, 1H), 7.45−7.34 (m, 4H), 6.51 (d, J = 8.7 Hz, 1H), 5.18 (br. s, 2H); MS (EI) m/z (rel intensity) 234 (13, $M^+ + 2$), 232 (38, M^+), 197 (19), 121 (100). Anal. Calcd for $C_{12}H_9ON_2$: C, 61.95; H, 3.90; N, 12.04. Found: C, 62.13; H, 3.89; N, 11.91.

Photoreaction of 2-Bromo-*N*-(2-pyridinyl)benzamide (3b). The photoreaction of **3b** (278 mg, 1 mmol) was performed for 5 h as described for **1a**. GC/MS analysis showed that there were three products, namely photoreduced (major), photocyclized, and photo-Fries-type products. The photoreduced product, **11** (82.2 mg, 42%) was purified by column chromatography (ϕ 2.2 cm × 25 cm, 70−230 mesh silica gel) with an eluent of EtOH/CH_3CN/$CHCl_3$ = 1/5/15: mp 80−81 °C (lit.[12a] mp 80−83 °C, lit.[12b] mp 82−84 °C); ^1H NMR (200 MHz, $CDCl_3$) δ 9.28 (br s, 1H), 8.41 (dd, J = 9.3, 0.9 Hz, 1H), 8.10 (dt, J = 4.9, 0.9 Hz, 1H), 7.93 (dt, J = 6.4, 1.7 Hz, 1H), 7.74 (dt, J = 1.5, 7.9 Hz, 1H), 7.59−7.42 (m, 3H), 7.01 (ddd, J = 7.3, 3.8, 0.9 Hz, 1H); MS (EI) m/z (rel intensity) 198 (12, M^+), 169 (53), 105 (100). Anal. Calcd for $C_{12}H_{10}ON_2$: C, 72.71; H, 5.08; N, 14.13. Found: C, 72.71; H, 5.05; N, 14.06.

Photoreaction of 2-Chloro-*N*-methyl-*N*-(4-pyridinyl)-benzamide (4). The photoreaction of **4** (110 mg, 0.4 m mole) was performed for 3 h as described for **1a**. TLC analysis showed that there was a photocyclized product, 5-(methyl)-benzo[*c*][1,6]naphthyridin-6(5*H*)-one (**16**), in high yield (85%, mp 174−175 °C); UV(λ_{max} in acetonitrile) 325 nm (ϵ = 6.25 × 10^3 L/mol·cm); IR ($CHCl_3$) 3071, 1663 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 8.58 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 6.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 6.83 (t, J = 8.0 Hz,), 6.66 (t, J = 7.5 Hz), 6.47 (d, J = 6.0 Hz), 2.62 (s, 3H); MS (EI) m/z (rel intensity) 210 (100, M^+), 181 (30), 154 (7). Anal. Calcd for $C_{13}H_{10}O_1N_2$: C, 74.27; H, 4.80; N, 13.32. Found: C, 74.17; H, 4.94; N, 12.94.

Kinetics. Measurement of Quantum Yield. The intensity of a Xe lamp at certain wavelengthes was measured by using standard ferrioxalate actinometry. Acetonitrile solutions of halobenzamide **1a**, **2a**, **3a**, and **4** (1.2×10^{-4} M) under argon or oxygen were irradiated by a Xe lamp at 270, 278, 282, and 250 nm for 5, 10, 6, and 5 min, respectively, whose intensities were 3.2, 4.5, 5.1, and 1.0×10^{15} quanta/s, respectively. The formation of the benzo[*c*]naphthyridinones are measured by the UV absorption changes at 322 (for **1a**), 340 (for **2a**), 334 (for **3a**), and 325 nm (for **4**), respectively. The quantum yields are shown at Tables 2 and 3.

For Stern−Volmer plots, the following procedure was performed: 2 mL of stock acetonitrile solution of **1a** (2.5×10^{-3} M, or **2a**) and 80 μL of 0.1 N NaOH aqueous solution were transferred into a 25 mL volumetric flask with 0, 0.1, 0.2, 0.3, 0.4, 0.5, and 0.6 mL of 0.1 M isoprene acetonitrile solution, respectively, and diluted to 25 mL with acetonitrile. The 3 mL of the solution was put into UV cuvette, deaerated with argon, and irradiated with monochromatic light at 270 nm for 10 min. The absorption change at 336 nm was monitored. The plot of Φ_o/Φ vs the concentration of isoprene yielded a straight line with an intercept of unit. The $K_Q\tau$ value was 194 M^{-1}. Assuming $K_Q = 6.4 \times 10^9$ M^{-1} s^{-1},[16] the lifetime of the triplet state of **1a** is 30 ns (lower limit).

Relative Rate of Photocyclization. Ten mL of 1.0 mM of **1a** in several solvents or in the solvent containing several reagents such as methyl methacrylate, Na_2CO_3, or NaOH was transferred into 15 mL quartz vessel and then deaerated with nitrogen for 20 min. After irradiation of the solution with monochromatic light and its treatment with NaOH for becoming slightly basic medium, the product formed in the reaction mixture was analyzed by GC (detector, FID). The relative rate of the formation of the products is shown in Table 4.

Laser Flash Photolysis. A detailed description of the experimental setup can be found elsewhere.[7a] The third and fourth harmonic (355 and 266 nm) outputs from a Q-switched Nd:YAG laser (Spectron SL852G-30) were used as excitation sources. The time duration of the excitation pulse was ca. 6 ns, and the pulse energy was typically 60 mJ. A cw Xe-lamp (Oriel model 6259, 300 W) was used as a probe light source for transient absorption measurement. The spectral resolution was obtained by using SP-275 monochromator (JAMS 27 model 82-49702) after the probe light passed through the sample solution. A boxcar signal averager (Standard Research System SR 250) was used in recording the transient signals. The temporal profile of the transient absorption signal was monitored by a 500 MHz digital storage oscilloscope (DSO, Tektronix TDS620B).

Sample solutions were prepared by dissolving the reactants in acetonitrile with or without tetramethylammonium chloride, and the concentration of the solution was adjusted to be 0.5−1.5 in absorbance at 266 nm. The experiment of the temporal profile with DSO was performed in the same concentration of **1a** in acetonitrile without tetramethylammonium chloride (insets in Figure 4). The sample solution was circulated from a reservoir (3 L in volume) to the fluorometer quartz cuvette of 10 mm in path length (Flow type, Helma QS 1.0) to reduce the effect of the accumulation of the product and dissociation of the reactant in the photolysis cell (Supporting Information).

The transient absorption spectra for chlorine in pyridine was measured with the experimental setup, shown in the Supporting Information. The method for the transient absorption is the same as above, except that chlorine is saturated into pyridine solution and the third harmonic (355 nm) laser was used for the photolysis.[23]

Energetics. Excitation spectra were obtained by scanning the excitation wavelength of light for the acetonitrile solution of **1a** (1.0×10^{-4} M) and measuring the fluorescence intensity at 342 nm (emission maximum). The fluorescence spectra was obtained by exciting the acetonitrile solution of **1a** (1.0×10^{-4} M) with 247-nm light and scanning the emission wavelength (Supporting Information). The phosphorescence spectra of **1a** was obtained in acetonitrile matrix with a luminescence spectrophotometer (Perkin-Elmer LS-50). The onset and the maximum of the phosphorescence are 363 and 425 nm, respectively.

The sensitizing behaviors of **1a** with triplet sensitizers such as acetone, acetophenone, and benzophenone were examined. The acetonitrile solution of **1a** (1 mL, 1.0×10^{-3} M) with 1 mL of acetonitrile solution of acetone (1.0×10^{-2} M), acetophenone (6.6×10^{-3} M), or benzophenone (3.3×10^{-3} M) in a 3 mL UV cell was deaerated with argon for 20 min and then irradiated for 2 h with monochromatic light (for acetone, acetophenone, and benzophenone, 325 ± 10 nm) at which only the sensitizer absorbed. The relative rate of the sensitizing reaction is shown in Table 6.

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Supporting Information Available: Experimental procedures for synthesis of 2-halo-*N*-pyridinylbenzamide (**1a**, **2a**, **3a**, **1b**, **2b**, **3b**, **1c**, **4**); Stern−Volmer plot of the intramloecular photocyclization of **1a** using the triplet quencher isoprene; excitation and emission spectra of **1a** in acetonitrile; experimental setup for the measurement of the transient absorption spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) The experiment for the detection of the n-complex of chlorine radical with pyridine should be carried out under a good hood system.