An Intramolecular Photosubstitution Reaction of N-(2,4-Dibromonaphthyl)-arenecarboxamide: Synthesis of 2-Arylnaphthoxazole

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Received March 3, 2003

Photoreactions of N-(2,4-dibromonaphthyl)arenecarboxamides in basic medium result in the intramolecular substituted products, 2-aryl-8-bromonaphthoxazoles in moderate yields and further photoreactions of the products afford the reduced products, 2-arylnaphthoxazoles. These reactions are straightforward for syntheses of naphthoxazole derivatives. Since the intramolecular photosubstitution of the bromoarenecarboxamide by the oxygen of its amide group is more effective than the photoreduction of the substituted product, 2-aryl-8-bromonaphthoxazole in basic medium, the intramolecular substituted product, 2-aryl-8-bromonaphthoxazole can be isolated. A charge-transfered excited singlet state of an imidol form of the 2-bromoarenecarboxamide is involved in the photosubstitution, whereas an excited triplet state of the 2-aryl-8-bromonaphthoxzole is closely involved in the photoreduction.

Key Words : Intramolecular photosubstitution, 2-Arylnaphthoxazole, N-(2,4-Dibromonaphthyl)benzamide, Charge-transferred excited singlet state, Photoreduction

Introduction

In 1999, we reported intramolecular photosubstitution reaction of N-(2-halophenyl)pyridinecarboxamide by its amide group.[1a] Photoreactions of N-(2-halo-phenyl)pyridine-carboxamides afforded 2-pyridylbenzoxazoles in basic medium. The substitution reaction occurs *via* an intramolecular aromatic electrophilic addition/elimination mechanism of the charge-transferred excited state from the imidolate anion of the N-(2-halophenyl)pyridinecarboxamide. We recently reported intramolecular photosubstitution reactions of 2'-halobenzanilides[1b] and N-(2-halophenyl)cyclohexane-carboxamides.[1c] Photoreaction of 2'-bromobenzanilide produced 2-phenylbenzoxazole in basic medium.[1b] Photoreaction of N-(2-halophenyl)cyclohexanecarboxamide led to 2-cyclohexyl-benzoxazole.[1c] These reactions are quite peculiar because the halogens of less reactive haloarenes toward nuclophilic aromatic substitution were displaced by oxygen of its amide groups. The reactions are also invaluable for benzoxazole ring formation. Thus, it is necessary to extend and generalize these reactions.

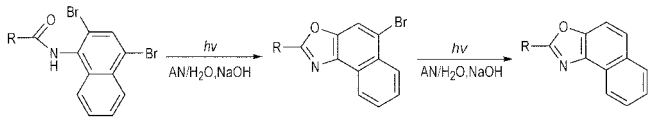
A few similar precedents have been reported. Ramakrishnan and coworkers described that intramolecular photosubstitution of o-halothioacetanilides afforded 2-methylbenzothiozoles.[2a] They proposed electron-transfer mechanism.[2b] Bowman and coworkers[3] described that intramolecular photosubstitution reactions of o-iodothiobenzanilide and o-iodothioacetanilide yielded 2-phenylbenzothiazole and 2-methylbenzothiazole, respectively. However, these reactions are not completely understood and generalized. This work describes that the intramolecular photosubstitution reactions occurred in the photoreactions of N-(2,4-dibromonaphthyl)-arenecarboxamides in acetonitrile and acetonitrile containing bases, and *in situ* photoreductions of the substituted products.

Results and Discussion

N-(2,4-Dibromonaphthyl)arenecarboxamides (**1**) were synthesized by aroylation of N-(2,4-dibromonaphthyl)amine. N-(2,4-Dibromonaphthyl)benzamide (**1a**) was prepared by benzoylation of 2,4-dibromonaphthylamine in pyridine. N-(2,4-Dibromonaphthyl)-4-pyridinecarboxamide (**1b**) and N-(2,4-dibromonaphthyl)-naphth-alene-2-carboxamide (**1c**) were prepared by aroylation of 2,4-dibromonaphthylamine with isonicotinic acid and 2-naphthoyl chloride, respectively. N-(2,4-Dibromonaphthyl)-N-methylbenzamide (**2**) was prepared by methylation of **1a**. Detail identification of these starting materials are given in the experimental section.

When an acetonitrile solution (450 mL) of N-(2,4-

Table 1. Product Yields from the Photoreaction of N-(2,4-Dibromonaphthyl)-arenecarboxamide (**1**) in several conditions



1a : R = phenyl
1b : R = pyridyl
1c : R = - naphthyl

3a
3b
3c

4a
4b
4c

substrate	solvent	irradiation time	Product	yield (%)
1a	AN/H_2O, NaOH	2 h	**3a**	31
			4a	42
	AN/H_2O, NaOH	10 min	**3a**	60
	AN	15 min	**3a**	40
	AN/H_2O, NaOH	3h	**4a**	33
1b	AN/H_2O, NaOH	15 min	**3b**	41
	AN/H_2O, NaOH	4 h	**4b**	32
1c	AN/H_2O, NaOH	15 min	**3c**	40
	AN/H_2O, NaOH	4 h	**4c**	25

dibromonaphthyl)benzamide (**1a**, 0.8 mmole) containing 50 mL of aqueous sodium hydroxide (2 M) was irradiated with a Hg-lamp (450 W) for 2 h, intramolecular substitution product, 2-phenyl-8-bromonaphth[1,2-d]oxazole (**3a**) and its reduced product, 2-phenylnaphth[1,2-d]oxazole (**4a**) were obtained in 31% and 42% yields, respectively (Table 1). No dark reactions were observed in this case and all other cases. Short irradiation (10 min) upon **1a** afforded only 2-phenyl-8-bromonaphth[1,2-d]oxazole (**3a**) in good yield (60%). In acetonilrile without base the photosubstitution reaction of **1a** occurred to give **3a** (40%). The intramolecular photosubstitution product was readily recognized by IR and MS spectra: imine (C = N) stretching appeared at 1486 cm^{-1} (KBr), whereas secondary amide N-H and carbonyl stretching of the starting material disappeared; characteristic molecular ion peaks containing one bromine appeared at m/z 325 (40%) and 323 (40%).

Longer irradiation (3 h) upon **1a** induced reduction of the intramolecular photosubstituted product (2-phenyl-8-bromonaphth[1,2-d]oxazole) formed initially, to give 2-phenylnaphth[1,2-d]oxazole in moderate yield (33%, Table 1). The structure of 2-phenylnaphth[1,2-d]oxazole was readily determined by MS and ^1H NMR spectra: a molecular ion peak without bromine atom was seen at m/z 245; two clear doublet peaks in aromatic region (δ 7.82 and 7.75) ppm were seen in place of an aromatic singlet peak (δ 8.11) of the photosubstituted product, **3a**.

When an acetonitrile solution of 2-bromonaphthylpyridinecarboxamide **1b** was irradiated with similar system for 15 min, 2-(4-pyridyl)-8-bromonaphth[1,2-d]oxazole (**3b**) was formed (41%, Table 1). Further irradiation of the reaction mixture produced 2-(4-pyridyl)naphth[1,2-d]oxazole (**4b**, 32%). Irradiation upon haloarene **1c** for 15 min gave 2-(β-naphthyl)-8-bromonaphth[1,2-d]oxazole (**3c**) in 40% yield. If the irradiation time was longer (4 h), 2-(β-naphthyl)-naphth[1,2-d]oxazole (**4c**) was obtained in 25% yield. Details for identification of these products are given in experimental section. These photoreactions are new and simple for the syntheses of derivatives of naphthoxazole, although several thermal reactions for the naphthoxazole ring formation are known.[4]

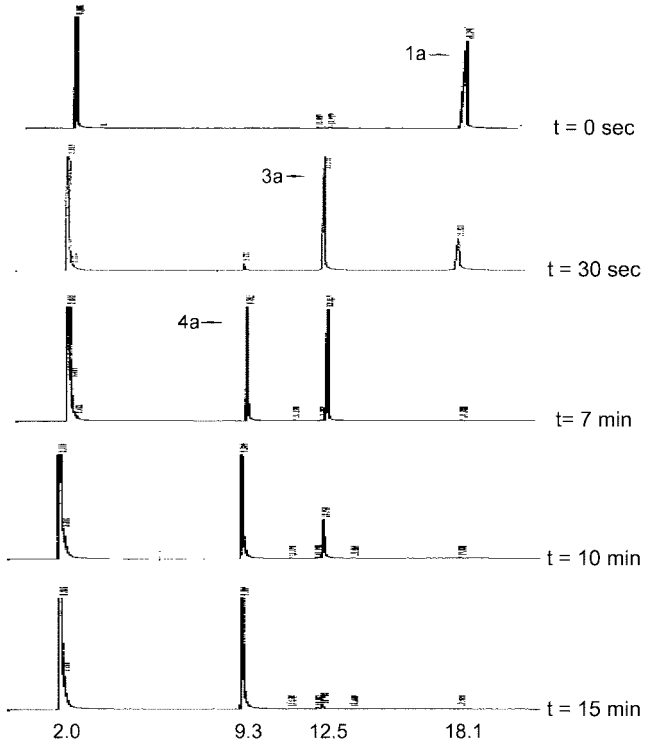


Figure 1. Changes of GC chromatogram vs irradiation time on the photoreaction of **1a** in acetonitrile containing aqueous NaOH.

In order to see reaction sequence, the product formation versus irradiation time was studied (see Figure 1). Before the reaction, the peaks at retention time 18.1 and 2.0 min on the GC chromatogram corresponded to starting material **1a** and acetonitrile, respectively. After photoreaction for 30 sec, the peak of **1a** decreased while a peak at retention time 12.5 min corresponding to intramolecular substitution product **3a** increased. For 7 min reaction time, both substituted products **3a** and reduced product **4a** (retention time 9.3 min) existed. For 10 min reaction time, **4a** increased while **3a** decreased. After 15 min, only reduced product was shown. These observations implies that intramolecular photosubstitution reaction is precedent to the photoreduction reaction of the intramolecular substituted product **3a**.

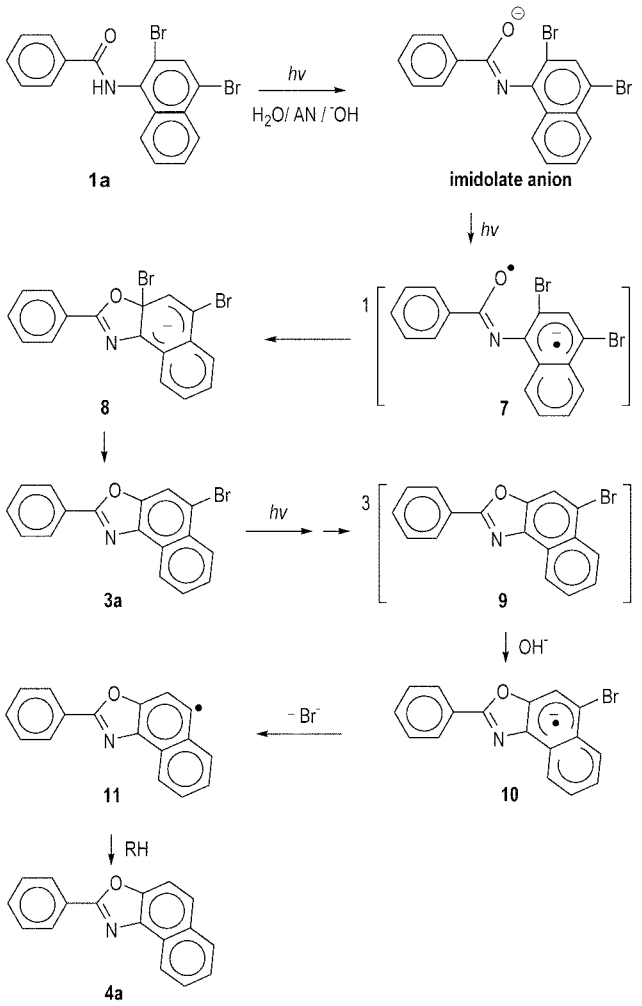
In order to clarify the reaction mechanism, the UV absorption behavior of **1a** was observed in the presence of NaOH and the reactivities were studied under several conditions (Table 2). The absorption maximum of **1a** appeared at 293 nm ($\varepsilon = 1.0 \times 10^4$ L/molecm) in acetonitrile. In the presence of NaOH (acetonitrile/2 M NaOH = 9/1) the absorption maximum moved to 327 nm (not shown) as in the case of N-(2-bromophenyl)pyridinecarboxamide.[1a] We believe that the new absorption maxium is responsible for the formation of the charge-transferred excited singlet state of imidolate anion of **1a**.

The relative rates of the formations of **3a** was 5 times greater in a basic medium than those in neutral medium acetonitrile (Table 2). In the presence of oxygen, the reduction was affected but substitution. These behaviors were also observed in the reaction of N-(2-halophenyl)pyridinecarboxamide.[1a] The oxygen effect implies that an excited singlet state is involved in the substitution, whereas an excited triplet state is closely related in the reduction. The effect of

Table 2. The Relative Rates of the product formation in the Photoreaction of N-(2,4-Dibromonaphthyl)benzamide (**1a**)[a] with a board spectrum of light from a Xenon lamp (400W)

solvent	atm	reaction time	relative rate	
			Substitution (**3a**)	Reduction (**4a**)
AN	N_2	1 h	1.0	0.1
AN/H_2O NaOH[b]	N_2	1 h	5.1	0.6
AN/H_2O NaOH[b]	O_2	1 h	5.0	0.2

[a]The concentration of the substrates used is 3×10^{-3} M. [b]AN:2M-NaOH = 8:2.



Scheme 1

base on the reaction can be explained by assuming the involvement of charge-transferred excited singlet state from the imidolate anion of **1a**.

The assumption was confirmed by observation of reactivities of N-(2,4-dibromonaphthyl)-N-methylbenzamide (**2**). The phototoreaction of **2** which can not exist as an imidolate form even in the presence of base produced a reduced product **5** only with minor photocyclized product **6** instead of the intramolecular photosubstituted product. Thus, this result implies that imidolate form is necessary for the substitution reaction.

We propose the following mechanism (Scheme 1). The charge-transferred excited singlet state **7** is populated by excitation of imidolate anion of **1a**. The singlet state **7** proceeds to anion **8** by addition of oxygen radical of the imidol anion to the carbon bearing bromine substituent of arene anion moiety. The anion **8** gives **3a** by eliminating bromide anion. This explanation is the same as that proposed for the intramolecular photosubstitution of N-(2-halopheny)-pyridine-carboxamide.[1a]

Reduction may occur by eliminating bromide ion from anion radical **10**, which is produced by charge-transfer to a triplet state of **3a** from base $^-$OH, to give a naphthyl radical **11** and then abstracting hydrogen atom of **11** to give final product **4a**. This explanation is known as electron-transfer mechanism for the photoreduction of haloarene.[5]

Experimental Section

Material and General procedure. α-Naphthylamine, isonicotinic acid, and 2-naphthoyl chloride (all Aldrich) were used without further purification. General procedure is the same as described elsewhere.[1a]

Synthesis of 2,4-Dibromonaphthylamine. In a 250 mL, three-necked, round-bottomed flask with a mechanical stirrer, dropping funnel, and condenser were placed 3.6 g (2.5 m mole) of -naphthylamine and 150 mL of chloroform. To the stirred solution was dropwise added 30 mL of chloroform solution of bromine (0.8 mL, 5 m mole). The mixture was stirred at 50 °C for one day. After evaporating the solvent, purple solids were collected. Crystallization from aqueous methanol gave 7.1 g (purple needle, 94%), mp 118 °C (lit 118 °C)[6]

Synthesis of N-(2,4-Dibromonaphthyl)benzamide (1a). To the pyridine solution of 2,4-dibromonaphthylamine (3 g/ 50 mL, 10 m mole) in 500 mL flask under ice/water bath, 1.4 mL of benzoyl chloride was added. The mixture was stirred at room temperature for one night. When 300 mL of water was added to the stirred mixture, white solids were obtained. Recrystallization from an aqueous ethanol gave 3.3 g (82%); mp 209 °C; UV (λ_{max} in CH_3CN) 233 nm ($\varepsilon = 1.6 \times 10^4$ L/ mole·cm), 293 nm ($\varepsilon = 1.1 \times 10^4$ L/molecm); IR (KBr) 3236, 1643, 1513 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, 1H, J = 8.5 Hz, C_5'-H), 8.06 (d, J = 8.5 Hz, 2H, $C_{2,6}$-H), 8.05 (s, 1H, C_3'-H), 7.95 (d, J = 8.5 Hz, 1H, C_8'-H), 7.81 (s, 1H, NH), 7.64 (t, J = 8.5 Hz, C_6'-H), 7.59 (t, J = 8.5 Hz, 1H, C_7'-H), 7.56 (m, 3H, $C_{3,4,5}$-H); MS m/z (rel intensity) 407 (2, M^-+4), 405 (3, M^++2), 403 (1, M^-), 326 (35), 105 (92).

Anal. Calcd for $C_{17}H_{11}ONBr_2$: C, 50.41; H, 2.74; N, 3.46. Found: C, 50.64; H, 2.72; N, 3.23.

Synthesis of N-(2,4-Dibromonaphthyl)-4-pyridinecarboxamide (1b). Isonicotinyl chloride was prepared by refluxing 2.5 g of isonicotinic acid in 20 mL of thionyl chloride for 2 h and then evaporating excess thionyl chloride. To isonicotinyl chloride prepared in situ were added 30 mL of pyridine and 7.5 g (0.0025 mole) of 2,4-dibromonaphthylamine. The mixture was stirred for one night. When 300 mL of water was added, white solids were obtained: Recrystallization from aqueous ethanol gave 5.4 g (67%): mp 184 °C; UV (λ_{max}, CH_3CN) 234 nm ($\varepsilon = 2.0 \times 10^4$ L/mole·cm); IR (KBr) 3221, 1647, 1516 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, J = 6.0 Hz, 2H, $C_{2,6}$-H), 8.25 (d, J = 8.3 Hz, 1H, C_5'-H), 8.04 (s, 1H, C_3'-H), 7.98 (s, 1H, NH), 7.86 (m, 3H, C_8'-H, $C_{3,5}$-H), 7.66 (t, J = 7.1 Hz, 1H, C_6'-H), 7.59 (t, J = 7.1 Hz, C_7'-H); MS m/z (rel intensity) 406 (2, M^-+1), 327 (50), 326 (48)

Anal. Calcd for $C_{16}H_{10}ON_2Br_2$: C, 47.33; H, 2.48; N, 6.90. Found: C, 47.17; H, 2.51; N, 6.74.

Synthesis of N-(2,4-Dibromonaphthyl)naphthalene-2-carboxamide (1c). A pyridine solution (3.3 mL) of 2-

naphthoyl chloride (1.9 g, 0.01 mole) and 2,4-dibromo-1-naphthylamine (3 g, 0.01 mole) was stirred for one night. When 150 mL of water was added to the mixture, white solids were obtained. Recrystallization from chloroform gave 4 g (90%): mp 242 °C; UV (λ_{max}, CH_3CN) 234 nm ($\varepsilon = 1.7 \times 10^4$ L/molecm); IR (KBr) 3221, 1642, 1518 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$)δ 8.60 (s, 1H, C_1-H), 8.26 (d, J = 8.4 Hz, 1H, C_3-H), 8.07 (s, 1H, C_3'-H), 8.00 (m, 6H, $C_{4,5,6,7,8}$-H and NH), 7.63 (m, 4H, $C_{5',6',7',8'}$-H); MS m/z (rel intensity) 457 (1, M^++4), 455 (2, M^-+2), 453 (1, M^-), 376 (60), 155 (100).

Anal. Calcd for $C_{21}H_{13}ONBr_2$: C, 55.42; H, 2.88; N, 3.07. Found: C, 55.31; H, 2.82; N, 2.93.

Synthesis of N-(2,4-Dibromonaphthyl)-N-methylbenzamide (2). In a 100 mL flask was dissolved 2 g of N-(2,4-dibromonaphthylbenzamide in 30 mL of acetone at 50 °C. To the warm solution were added 1.2 g of potassium hydroxide power and 1.2 g of methyl iodide (8 m mole) and the mixture was refluxed for 2 h. After evaporation of solvent and excess methyl iodide, 50 mL of water was added to the residue. The mixture was extracted with chloroform. A column chromatography with *n*-hexane/ethyl acetate and crystallization from aqueous ethanol gave 1.5 g of N-(2,4-dibromonaphthyl)-N-methylbenzamide (70%): mp 120-121 °C; UV (λ_{max}, CH_3CN) 234 nm ($\varepsilon = 1.9 \times 10^4$ L/molecm); IR (KBr) 3029, 2942, 1653, 1566, 1384 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H, C_5'-H) 8.02 (d, J = 8.0 Hz, 1H, C_8'-H), 7.70 (s, 1H, c_3'-H) 7.66 (m, 2H, $C_{6',7'}$-H), 7.30 (d, J = 8.0 Hz, 2H, $C_{2,6}$-H), 7.16 (t, J = 7.5 Hz, 1H, C_4-H), 7.00 (t, J = 7.5 Hz, 2H, $C_{3,5}$-H), 3.44 (s, 3H, CH_3); MS, m/z (rel intensity) 421 (1, M^-+4), 419 (1, M^-+2), 105 (100).

Anal. Calcd for $C_{18}H_{13}ONBr_2$: C, 51.58; H, 3.13; N, 3.34. Found: C, 51.26; H, 3.07; N, 3.15.

Preparative photoreaction: Photoreaction of N-(2,4-Dibromonaphthyl)benzamide (1a). To a large quartz immersion well photolysis unit with provision for circulation of nitrogen were added 450 mL of acetonitrile, 326 mg of N-(2,4-dibromonaphthyl)benzamide (**1a**, 0.8 m mole), and 50 mL of aqueous sodium hydroxide (2 M). With nitrogen circulation, the mixture was irradiated with a 450 W mercury lamp (medium pressure) for 2 h. After evaporation of acetonitrile, the mixture was extracted with diethyl ether. The mixture was chromatographed (silica gel 60, 32 × 3 cm) with 3 : 1 *n*-hexane/ethyl acetate to give 92 mg of 2-phenylnaphth[1,2-d]oxazole and 69 mg of 2-phenyl-8-bromonaphth[1,2-d]oxazole. Crystallization from agueous ethanol gave 82 mg of 2-phenylnaphth[1,2-d]oxazole and 58 mg of 2-phenyl-8-bromo-naphth[1,2-d]oxazole. When the irradiation time was longer (3 hr) than 2 h, 2-phenylnaphth-[1,2-d]oxazole was only obtained (33%). When the irradiation time is short (10 min), 2-phenyl-8-bromonaphth[1,2-d]-oxazole was only formed (60%).

2-Phenyl-8-bromonaphth[1,2-d]oxazole (3a): Yield 58 mg (31%); mp 176 °C; UV (λ_{max}, CH_3CN) 350 nm ($\varepsilon = 2.5 \times 10^4$ L/mole·cm); IR (KBr) 3054, 1578, 1486, 777, 712 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 8.1 Hz, 1H) 8.36 (d, J = 8.1 Hz, 1H), 8.32(d, J = 6.5 Hz, 2H) 8.10 (s, 1H), 7.72 (t, J = 8.1 Hz, 1H), 7.65 (t, J = 8.1 Hz, 1H), 7.55 (m, 3H); MS, m/z (rel intensity) 325 (40, M^-+2), 323 (40, M^-).

Anal. Calcd for $C_{17}H_{10}ONBr$: C, 62.99; H, 3.11; N, 4.32. Found: C, 63.01; H, 3.12; N, 4.34.

2-Phenylnaphth[1,2-d]oxazole (4a): Yield 82 mg (42%): mp 125 °C; UV (λ_{max}, CH_3CN) 343 nm ($\varepsilon = 1.7 \times 10^4$ L/molecm); IR (KBr) 3048, 2924, 1550, 1486, 707 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.0 Hz, 1H) 8.34 (m, 2H), 7.98 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.56 (m, 1H), 7.55 (m, 3H); MS, m/z (rel intensity) 245 (M^-, 100).

Anal. Calcd for $C_{17}H_{11}ON$: C, 83.25; H, 4.52; N, 5.71. Found: C, 83.45; H, 4.63; N, 5.60.

Photoreaction of N-(2,4-Dibromonaphthyl)-4-pyridinecarboxamide (1b). The irradiation of N-(2,4-dibromonaphthyl-4-pyridinecarboxamide (**1b**) for 15 min in the same procedure as in the case of **1a** gave 2-(4-pyridyl)-8-bromonaphth[1,2-d]oxazole (41%). When the irradiation time was 4h, 2-(4-pyridyl)naphth[1,2-d]oxazole was only obtained (32%).

2-(4-Pyridyl)-8-bromonaphth[1,2-d]oxazole (3b): mp 180 °C; IR (KBr) 3049, 1602, 1577, 1479 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.84 (d, J = 6.6 Hz, 2H), 8.62 (d, J = 7.8 Hz, 1H), 8.39 (d, J = 7.8 Hz, 1H) 8.15 (d, J = 6.0 Hz, 2H), 8.14 (s, 1H), 7.77 (t, J = 7.8 Hz, 1H), 7.70 (t, J = 7.8 Hz, H); MS, m/z (rel intensity) 326 (100, M^-+2), 324 (100, M^-).

Anal. Calcd for $C_{16}H_9ON_2Br$: C, 59.10; H, 2.79; N, 8.62. Found: C, 59.20; H, 2.80; N, 8.54.

2-(4-Pyridyl)naphth[1,2-d]oxazole (4b): mp 166 °C; IR (KBr) 3171, 3047, 1602, 1485 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.84 (d, J = 5.4 Hz, 2H), 8.60 (d, J = 7.5 Hz, 1H), 8.17 (m, 2H), 8.00 (d, J = 8.4 Hz, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.76 (d, J = 9.0 Hz, 1H), 7.72 (t, J = 8.1 Hz, 1H), 7.60 (t, J = 8.1 Hz, 1H); MS, m/z (rel intensity) 246 (100, M^-).

Anal. Calcd for $C_{16}H_{10}ON_2$: C, 78.04; H, 4.09; N, 11.38. Found: C, 78.16; H, 4.18; N, 11.47.

Photoreaction of N-(2,4-Dibromonaphthyl)naphthalene-2-carboxamide (1c). Photoreaction of N-(2,4-Dibromonaphthyl-2-naphthalenecarboxamide in base medium for 15 min produced 2-(β-naphthyl)-8-bromonaphth[1,2-d]oxazole (40%). When the irradiation time was 4 h, 2-(β-naphthyl)-naphth[1,2-d]oxazole was only obtained (25%).

2-(β-naphthyl)-8-bromonaphth[1,2-d]oxazole (3c): mp 210 °C; IR (KBr) 3055, 1631, 1579, 1545, 1346 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.83 (s, 1H) 8.65 (d, J = 7.8 Hz, 1H), 8.41 (d, J = 5.0 Hz, 1H), 8.38 (d, J = 5.0 Hz, 1H), 8.16 (s, 1H), 8.02 (m, 2H), 7.90 (m, 1H), 7.68 (t, J = 7.2 Hz, 1H), 7.75 (t, J = 7.2 Hz, 1H), 7.59 (m, 2H); MS, m/z (rel intensity) 375 (100, M^-+2), 373 (100, M^-).

Anal. Calcd for $C_{21}H_{12}ONBr$: C, 67.40; H, 3.23; N, 3.74. Found: C, 67.23; H, 3.20; N, 3.85.

2-(β-naphthyl)naphth[1,2-d]oxazole (4c): mp 154 °C; IR (KBr) 3049, 2918, 1539, 1444 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.63 (d, J = 8.1 Hz, 1H), 8.42 (d, J = 8.7 Hz, 1H) 8.01 (m, 3H), 7.84 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 8.7 Hz, 1H), 7.70 (t, J = 7.2 Hz, 1H), 7.59 (m, 1H), 7.58

(m, 3H); MS, m/z (rel intensity) 295 (100, M^+).

Anal. Calcd for $C_{21}H_{13}ON$: C, 85.40; H, 4.44; N, 4.74. Found: C, 85.61; H, 4.40; N, 4.80.

Photoreaction of N-(2,4-dibromonaphthyl)-N-methylbenzamide (2). Irradiation of N-(2,4-dibromonaphthyl)-N-methylbenzamide (**2**, 188 mg) for 2 h in the same procedure as in the case of **1a** gave N-methyl-N-naphthylbezamide (**5**), and N-methylbenz[f]phenanthridone (**6**) in 14% and 30% yield, respectively.

N-Methyl-N-naphthylbenzamide (5): Yield 16.4 mg (14%): mp 119 °C; UV (λ_{max}, CH_3CN) 286 nm ($\varepsilon = 2.0 \times 10^4$ L/mole·cm); IR (KBr) 3056, 2935, 1640, 1593 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 8.1 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.62 (m, 3H), 7.24 (m, 3H), 7.09 (m, 4H), 3.54 (s, 3H); MS, m/z (rel intensity) 261 (50%, M^-), 105 (100%).

Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.61; H, 5.41; N, 5.30.

N-Methylbenz[f]phenanthridone (6): Yield 34.8 mg (30%): mp 136 °C; UV (λ_{max}, CH_3CN) 367 nm ($\varepsilon = 4.4 \times 10^4$ L/mole·cm); IR (KBr) 3059, 3045, 2960, 1646, 1608, 1312 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 8.1 Hz, 1H) 8.30 (m, 3H), 7.80 (m, 6H), 4.07 (s, 3H); MS, m/z (rel intensity) 259 (80%, M^+), 258 (100%, M^--1).

Anal. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.40; H, 5.10; N, 5.42.

Reaction sequence. An acetonitrile solution of **1a** containing 2 M-NaOH was irradiated under nitrogen as in the case of the preparative photoreaction of **1a**. A small portion of the reaction solution (20 μL), periodically withdrawn, was analyzed on GC (Hewlett-Packard 4890) using a capillary column (30 m × 0.25 mm × 2.25 μm) containing crosslinked PHME. The temperature on oven increased a rate 10 °C per minute from 200 °C to 280 °C. The temperature of injection and detection pots were 240 and 280 °C, respectively.

Kinetic experiment. An acetonitrile solution of **1a** with/without 2 M NaOH (3.0×10^{-3} M, 2 mL) was prepared in UV cuvetle cell (path length 1 cm), deaerated by nitrogen (or aerated by oxygen), and irradiated by 400 W Xe-lamp for 1 hr. A small portion of the solution (5 μL) was analyzed on GC using the capillary column. The relative rate was measured by comparing the peak area on the GC chromatograph.

Acknowledgment. This work was supported by Korea Research Foundation Grant (KRF-2002-005-C00009).

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