

Yong-Tae Park, Ick-Hyung Lee and Young-Hee Kim

Department of Chemistry, Kyungpook National University
Taegu, 702-701, Korea
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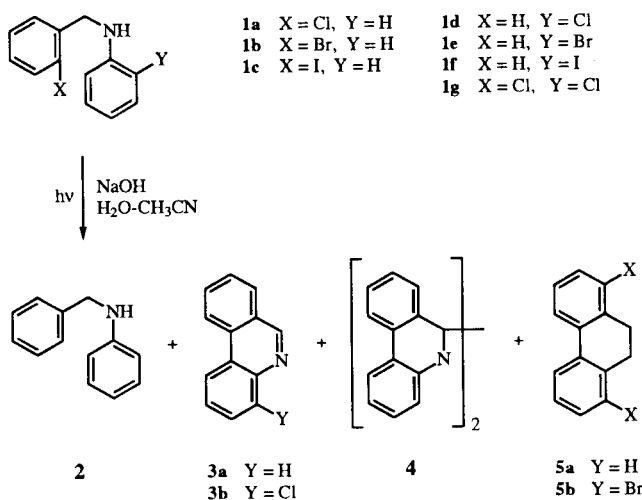
Several *N*-(2-halobenzyl)anilines and *N*-benzyl-2-haloanilines have been synthesized and their photochemical reactions studied. Upon irradiation, the aqueous acetonitrile solution of *N*-benzyl-2-chloroaniline was cyclized and reduced to give phenanthridine, 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl (THBP), *N*-benzylaniline, and bibenzyl. Similar products were produced in the photochemical reactions of other halogenated *N*-benzylanilines, except iodo-substituted *N*-benzylanilines. No dimer (THBP) was produced from the iodo-substituted *N*-benzylanilines. Both singlet and triplet states are involved in the photochemical reactions of the haloarenes.

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Introduction.

The photochemistry of halogenated arenes is of considerable importance in organic syntheses and in degrading halogenated arenes which pollute the environment. Sakurai and his collaborator [1] reported that upon irradiation *N*-(2-chlorobenzyl)aniline (**1a**) and *N*-(2-bromobenzyl)aniline (**1b**) produced phenanthridine and 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl in the presence of sodium hydroxide (see Scheme 1). We reported that upon irradiation *N*-(2-iodobenzyl)aniline (**1c**) gave phenanthridine and a trace amount of 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl [2]. On the basis of these results a study was performed using a series of *N*-benzyl-2-haloanilines to clarify their photochemical properties.

Scheme 1



chloroaniline (**1d**) in the presence of sodium hydroxide was irradiated with a high pressure Hg lamp photocyclized products, phenanthridine (**3a**), 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl (**4**), and two photoreduced products, *N*-benzylaniline (**2**) and bibenzyl (**5a**) were obtained (see Scheme 1 and Table 1). The products, phenanthridine and *N*-benzylaniline were easily identified with authentic materials. 5,5',6,6'-Tetrahydro-6,6'-biphenanthridyl was identified by mp measurement, ir, nmr, and mass spectra. The singlet at 4.70 ppm in nmr spectra is assigned to protons on the sp³ carbons. The multiplet at 6.70-9.20 ppm is assigned to protons on the aromatic rings. The ratio of the singlet to the multiplet is 1/8. A melting point measurement (175-183°) [1] confirms the structure **4**.

Bibenzyl was identified with uv, nmr and mass spectra. The singlet at 2.98 ppm is assigned to protons on the sp³-carbons. The multiplet at 7.20-7.50 ppm is assigned to protons on aromatic rings. The ratio of the singlet to the multiplet is 2/5. A melting point measurement (51- 52°) confirms the structure **5a**.

The photochemical reaction products and their yields of the halogenated *N*-benzylanilines are summarized in Scheme 1 and Table 1. These results show that the photocyclization reactions occur for *N*-benzylanilines halogenated on the *N*-phenyl ring as well as on the *C*-phenyl ring. Iodo-substituted *N*-benzylanilines produced phenanthridine but almost no dimer **4**. The photocyclization of

Table 1
Yields of the Photochemical Reactions

Reactants	Product Yield (%)				
	2	3a	3b	4	5a 5b
1a	3	37		10	
1b	0	37		8	8
1c	3	43		1	
1d	8	14		10	10
1e	5	10		16	6
1f	9	41		0	0
1g	8		3	2	

Results and Discussion.

(a) Preparative Photochemical Reactions.

When an aqueous acetonitrile solution of *N*-benzyl-2-

1c and **1f** in the presence of sodium hydroxide is a good method for phenanthridine synthesis.

We carefully examined *N*-(2-chlorobenzyl)anilines (**1a**) and *N*-(2-bromobenzyl)aniline (**1b**). In the photochemical reactions of **1a** in acetonitrile in the presence of sodium hydroxide, photoreduced product, **2** as well as **3a** and **4** could be observed. When the aqueous acetonitrile solution of **1a** in the absence of sodium hydroxide was irradiated, a polymerized material and small amount of *N*-benzylaniline as well as **3a** and **4** are obtained. In the case of **1b**, with sodium hydroxide, bi-(2,2'-dibromo)benzyl (**5b**) was obtained in addition to **2**, **3**, and **4**.

(b) Kinetic Studies.

We reproduced Mizuno's experiment [1] for the identification of 5,6-dihydrophenanthridine as a reaction intermediate in photocyclization of *N*-(2-chlorobenzyl)aniline and obtained the same results.

The initial quantum yield of the photocyclization of the halogenated *N*-benzylanilines in the presence or absence of oxygen was determined and is summarized in Table 2. In general, the quantum yield of the reaction is low. The quantum yield of the photocyclization of **1a** is higher than **1b**, even though the bond energy of aromatic C-Cl is stronger than C-Br. There should be an assistance of π -complexation of halogen with the aryl ring in the reaction similar to the photocyclization of the 2-bromopyridinium salt [3]. The photocyclization of chloro- and bromo-substituted benzylanilines are quenched somewhat by the presence of oxygen. However, that of iodo-substituted benzylaniline is assisted slightly in the presence of oxygen. Iodo-substituted *N*-benzylaniline gave a high quantum yield for the photocyclization. In the case of iodo-substituted *N*-benzylaniline, free phenyl radicals which formed from cleavage of C-I bond could be formed from both the singlet and triplet states because of the weak bond of C-I.

Table 2

Quantum Yield for the Photocyclization of the Halogenated *N*-Benzylanilines in Aqueous Acetonitrile with/without O₂ in the Presence of Sodium Hydroxide

Reactants	λ max (nm) (ϵ)	Quantum Yield ($\Phi \times 10$)	
		without O ₂	with O ₂
1a	295 (2470)	0.095	0.084
1b	294 (2590)	0.079	0.068
1c	293 (2630)	0.74	0.77
1d	299 (3090)	<0.01	<0.01
1e	301 (3200)	<0.01	<0.01
1f	303 (3340)	0.15	0.36
1g	298 (3040)	0.01	<0.01

The Stern-Volmer plot for the photocyclization of *N*-(2-chlorobenzyl)aniline (**1a**) in deaerated acetonitrile was obtained (see Figure 1). In the presence of naphthalene

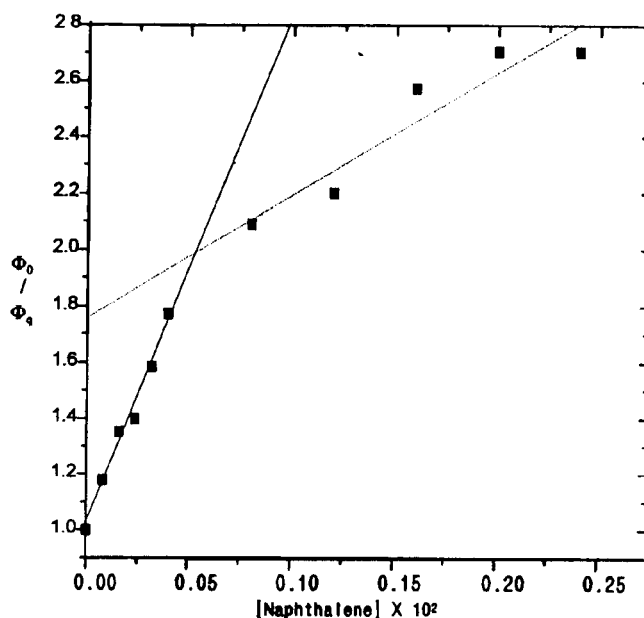


Figure 1. The Stern-Volmer plot for the photocyclization of *N*-(*o*-chlorobenzyl)aniline (**1a**) in deaerated acetonitrile with naphthalene as the quencher. [**1a**] = 8×10^{-4} M.

only part of the reaction was quenched. That is, a plot of Φ_0/Φ_q vs. $[Q]$ is initially linear with a steep slope at low quencher concentrations. As $[Q]$ is increased, a gradual decrease in the slope occurs until a final linear region is attained (see Figure 1). The initial slope at a low quencher concentration is attributed to normal triplet quenching. The final slow slope is attributed to singlet quenching at a higher quencher concentration. These results show that the photocyclization occurs from both the singlet and triplet excited states of these molecules. From the steep slope of the linear Stern-Volmer plot obtained and the assumed $k_q = 2 \times 10^{10} \text{ M}^{-1}\text{S}^{-1}$ in acetonitrile [4], a triplet lifetime of 92 n sec was obtained. From the low slope of the plot obtained and the assumed $k_q = 2 \times 10^{10} \text{ M}^{-1}\text{S}^{-1}$ in acetonitrile [4], a singlet lifetime of 22 n sec was obtained. A similar Stern-Volmer plot for the photocyclization of *N*-(2-bromobenzyl)aniline (**1b**) in deaerated acetonitrile with naphthalene was also obtained.

When the aqueous acetonitrile solution of **1a** in the presence of sodium hydroxide was irradiated, a new imine stretching (1658.9 cm^{-1}) was observed in the ir (see Figure 2). This infers that imine **7** is an intermediate in the formation of the dimer. Thus we propose a mechanism for the photocyclization of **1** in Scheme 2.

With light absorption the halogenated *N*-benzylanilines produce singlet states. The singlet states competitively undergo by three routes: triplet states via an intersystem crossing, free benzyl radicals by bond cleavage of C-H bond, and free phenyl radical by the cleavage of the C-X bond.

period of 0.5 hour. The reaction mixture was maintained at this temperature with stirring for 2 hours and cooled. The organic layer was separated, washed with saturated aqueous sodium chloride solution and dried over sodium sulfate anhydrous. The crude product was purified by vacuum distillation.

N-(2-Chlorobenzyl)aniline (**1a**).

This material was isolated in 74% yield (3.2 g) as yellowish liquid, bp 130-133°/0.45 mm Hg, lit 160-163°/4 mm Hg [1]; ir (potassium bromide): ν 3440 cm^{-1} (NH); uv (ethanol): λ max 296.2 (2470) nm; ^1H nmr (chloroform- d_1): δ 3.90 (s, 1H, NH), 4.31 (s, 2H, CH_2), 6.50-7.60 (m, 9H, aromatic); ms: m/z (relative abundance) 219 ($\text{M}^+ + 2$, 32%), 217 (M^+ , 98%).

N-(2-Bromobenzyl)aniline (**1b**).

This material was isolated in 79% yield as yellowish liquid (5 g), bp 165-167°/0.4 mm Hg, lit 184-189°/7 mm Hg [1]; ir (potassium bromide): ν 3393 cm^{-1} (NH); uv (ethanol): λ max 293.4 (2590) nm; ^1H nmr (chloroform- d_1): δ 3.60 (s, 1H, NH), 4.41 (s, 2H, CH_2), 6.60-7.61 (m, 9H, aromatic); ms: m/z (relative abundance) 263 ($\text{M}^+ + 2$, 98%), 261 (M^+ , 100%).

N-(2-Iodobenzyl)aniline (**1c**).

This material was isolated in 56% yield as colorless crystals, mp 61-62°; ir (carbon tetrachloride): ν 3430 cm^{-1} (NH); uv (ethanol): λ max 292.8 (2630) nm; ^1H nmr (chloroform- d_1): δ 4.21 (s, 1H, NH), 4.35 (s, 2H, CH_2), 6.62-7.90 (m, 9H, aromatic); ms: m/z (relative abundance) 309 (M^+ , 100%).

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{NI}$: C, 50.51; H, 3.91; N, 4.53. Found: C, 50.62; H, 3.85; N, 4.40

N-Benzyl-2-chloroaniline (**1d**).

This material was isolated in 83% yield as colorless crystal (13.6 g), mp 36-38°; ir (chloroform): ν 3422 cm^{-1} (NH); uv (ethanol): λ max 298.4 (3090) nm; ^1H nmr (chloroform- d_1): δ 4.41 (s, 2H, CH_2), 4.70 (s, 1H, NH), 6.61-7.30 (m, 9H, aromatic); ms: m/z (relative abundance) 219 ($\text{M}^+ + 2$, 13%), 217 (M^+ , 42%).

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{NCl}$: C, 71.72; H, 5.56; N, 6.43. Found: C, 71.72; H, 5.75; N, 6.50.

N-Benzyl-2-bromoaniline (**1e**).

This material was isolated in 85% yield as colorless crystals (1.6 g), mp 34-35°; ir (chloroform): ν 3416 cm^{-1} (NH); uv (ethanol): λ max 300 (3200) nm; ^1H nmr (chloroform- d_1): δ 4.30 (s, 2H, CH_2), 4.71 (s, 1H, NH), 6.51-7.40 (m, 9H, aromatic); ms: m/z (relative abundance) 263 ($\text{M}^+ + 2$, 48%), 261 (M^+ , 50%).

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{NBr}$: C, 59.56; H, 4.61; N, 5.34. Found: C, 59.77; H, 4.80; N, 5.45.

N-Benzyl-2-iodoaniline (**1f**).

For the synthesis of this compound, benzene-water solvent is used in the general procedure. This material was isolated in 73% yield as colorless crystals, mp 23°; ir (potassium bromide): ν 3402 cm^{-1} (NH); uv ethanol: λ max (ϵ) 303 (3340) nm; ^1H nmr (chloroform- d_1): δ 4.30 (s, 2H, CH_2), 4.61 (s, 1H, NH), 6.80-7.93 (m, 9H, aromatic); ms: m/z (relative abundance) 309 (M^+ , 72%).

Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{NI}$: C, 50.51; H, 3.91; N, 4.53. Found: C, 50.82; H, 4.05; N, 4.60.

N-(2-Chlorobenzyl)-2-chloroaniline (**1g**).

This material was isolated in 87% yield as colorless crystals, mp 43°; ir (carbontetrachloride): ν 3470 cm^{-1} (NH); uv

(ethanol): λ max (ϵ) 298.8 (3040) nm; ^1H nmr (chloroform- d_1): δ 4.51 (s, 2H, CH_2), 4.80 (s, 1H, NH), 6.50-7.40 (m, 8H, aromatic); ms: m/z (relative abundance) 255 ($\text{M}^+ + 4$, 3%), 253 ($\text{M}^+ + 2$, 20%), 251 (M^+ , 30%).

Anal. Calcd. for $\text{C}_{13}\text{H}_{11}\text{NCl}_2$: C, 61.93; H, 4.40; N, 5.56. Found: C, 62.05; H, 4.54; N, 5.61.

General Procedure for Preparative Photochemical Reaction of *N*-Benzylaniline Halogenated in the Presence of Sodium Hydroxide (Method A).

Into a water cooled pyrex immersion well under nitrogen was placed 4.6 mmoles of *N*-(2-chlorobenzyl)aniline, 500 ml of acetonitrile-water (9:1), and 0.18 g of sodium hydroxide. The reaction mixture was irradiated with a 200 W Hg lamp for 20 hours. The reaction was followed by the increasing absorption peak around 343 nm. After removal of the solvent, the residue was dissolved in diethyl ether (200 ml), washed with water and dried with magnesium sulfate. After stripping the solvent, the residue was separated on tlc (silical gel, eluent, benzene:acetone = 20:1).

Photochemical Reaction of *N*-(2-Chlorobenzyl)aniline (**1a**).

Three bands on tlc appeared. The R_f value are 0.2, 0.8, and 0.9 and identified as phenanthridine (37%, 305 mg), 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl (10%, 83 mg) and *N*-benzylaniline (3%, 25 mg). The product of $R_f = 0.2$ was identified as phenanthridine with the following data; mp 104-105° (lit 105-106° [1,5]); uv (ethanol): λ max 343 nm; ^1H nmr (chloroform- d_1): δ 7.20-9.32 (m, aromatic); ms: m/z (relative abundance) 179 (M^+ , 100%), 152 (C_{12}H_8 , 8%).

The product of $R_f = 0.8$ was identified as 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl with following data, mp 175-184° (lit 175-185° [1,5]); ir (potassium bromide): ν 3373 cm^{-1} (NH); ^1H nmr (chloroform- d_1): δ 4.70 (s, 2H, CH_2), 7.20-9.31 (m, 8H, aromatic); ms: m/z (relative abundance) 360 (M^+ , 1%), 180 ($\text{C}_{13}\text{H}_{10}\text{N}^+$, 100%).

The product of $R_f = 0.9$ was identified as *N*-benzylaniline, yield 3%, mp 35-36° (lit 36° [6]); ir (potassium bromide): ν 3410 cm^{-1} (NH); uv (ethanol): λ max 295.2 nm; ^1H nmr (chloroform- d_1): δ 3.70 (s, 1H, NH), 4.31 (s, 2H, CH_2), 6.61-7.41 (m, 10H, aromatic); ms: m/z (relative abundance) 183 (M^+ , 76%).

Photochemical Reaction of *N*-(2-Bromobenzyl)aniline (**1b**).

2,2'-Dibromobenzyl was isolated in 8% yield in addition to **3a** (37%) and **4** (8%). The three bands on tlc appeared. Two major compounds with $R_f = 0.2$ and $R_f = 0.85$ were identified as phenanthridine (37% yield) and 5,5',6,6'-tetrahydro-6,6'-biphenanthridyl respectively. The second compound with $R_f = 0.7$ was characterized as 2,2'-dibromobenzyl (8% yield) by the following data, mp 77-79°; ^1H nmr (chloroform- d_1): δ 3.04 (s, 4H, 2 CH_2), 6.90-7.54 (m, 8H, aromatic); ms: m/z (relative abundance) 342 ($\text{M}^+ + 4$, 49%), 340 ($\text{M}^+ + 2$, 100%), 338 (M^+ , 50%).

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{Br}_2$: C, 49.45; H, 3.56. Found: C, 49.45; H, 3.67.

Photochemical Reaction of *N*-(2-Iodobenzyl)aniline (**1c**).

Phenanthridine (43% yield) and *N*-benzylaniline (3%) were isolated.

Photochemical Reaction of *N*-Benzyl-2-chloroaniline (**1d**) and *N*-Benzyl-2-bromoaniline (**1e**).

Bibenzyl (10% yield) in addition to **2**, **3a**, and **4** was isolated, mp 51-52°; uv: λ max 292, 240 nm; ^1H nmr (chloroform- d_1): δ 2.98 (s, 4H, 2CH₂), 7.20-7.50 (m, 10H, aromatic); ms: m/z (relative abundance) 182 (M⁺, 30%).

Photochemical Reaction of *N*-Benzyl-2-iodoaniline (**1f**).

Phenanthridine (41%) and *N*-benzylaniline (9%) were isolated.

Photochemical Reaction of *N*-(2-Chlorobenzyl)-2-chloroaniline (**1g**).

4-Chlorophenanthridine (**3b**, 3%) in addition to **2** (8%) and **4** (2%) were isolated.

Preparative Photochemical Reaction of *N*-(2-Chlorobenzyl)-aniline without Sodium Hydroxide (Method B).

The procedure is the same as Method A except for the absence of sodium hydroxide. *N*-Benzylaniline only was isolated in 23% yield. The major product was a polymer-like substance which was unidentified.

Detection of an Imine Group as the Intermediate.

Nine milliliters of an acetonitrile solution of **1a** (1×10^{-3} M) in the presence of sodium hydroxide (1×10^{-3} M) was placed in a quartz cuvette and irradiated with monochromatic light (at 295 nm) for 10 minutes. Ether was added to the reaction mixture and then the mixture was washed three times with water to eliminate the alkali. The mixture was dried to give a solid. A potassium bromide disk with the product solid was prepared for the ir spectroscopy. An imine stretching frequency at 1658.8 cm^{-1} could be observed.

Kinetic Study.

Three milliliters of an appropriate concentration of the halogenated *N*-benzylaniline (1×10^{-4} M) in acetonitrile was placed in a uv cuvette (1 cm path) and deaerated with argon or aerated with oxygen for 20 minutes. At the beginning no absorption at

343 nm was observed, which means the initial product, 5,6-dihydrophenanthridine was not formed. The solution in the cuvette was irradiated with monochromatic light (at 295 nm light for the case of **1a**, ± 5 nm band pass) for 20 minutes. An absorption on 343 nm appeared. Thus, the concentration of the product, 5,6-dihydrophenanthridine depending irradiating time could be measured using the molecular absorptivity of 5,6-dihydrophenanthridine ($\epsilon = 4040 \text{ l/mole}\cdot\text{cm}$). The initial quantum yield for the **1a-1g** is shown in Table 2. In order to examine the excited state of *N*-(2-chlorobenzyl)aniline (**1a**), the triplet quencher, naphthalene was used. When the acetonitrile solutions of **1a** (8×10^{-4} M) in the presence of naphthalene (0, 0.8, 1.6, 2.4, 3.2, 4.0, 8.0, 12, 16, 20, 24 $\times 10^{-4}$ M) were irradiated with monochromatic light, quantum yields (0.0211, 0.0179, 0.0156, 0.0151, 0.0133, 0.0119, 0.0101, 0.0096, 0.0082, 0.0078, and 0.0078 respectively) were observed. The Stern-Volmer plot is shown in Figure 2.

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