

## THE PHOTOCHEMICAL REACTION OF 1-HALO-2-(PHENYLALKYL)BENZENES

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**Abstract**—Haloarene in which the phenyl group and halophenyl group are connected by alkyl groups were synthesized to study the photochemical behavior. The photochemical reactions of 1-halo-2-(phenylalkyl)benzenes (**1** and **2**) were studied in several aerated or unaerated solvents. In the case of 2-benzyl-1-halobenzene photoreduced product (biphenyl) is major in acetonitrile or benzene. In cyclohexane or acetonitrile with triethylamine, photoreduced product is obtained exclusively, while in acetonitrile with toluene, xylene, or sodium hydroxide photocyclized product (fluorene) is mainly obtained. In the case of 1-halo-2-phenethylbenzenes (**5** and **6**), photocyclized product (9,10-dihydrophenanthrene and phenanthrene) are major in acetonitrile or benzene. While the haloarenes **1** or **2** connecting the two arene rings by methylene is photoreduced, the other haloarene **5** or **6** connecting by ethylene is photocyclized. In cyclohexane or acetonitrile with a small amount of triethylamine, photoreduced reactions of **5** or **6** mainly occur. In acetonitrile with sodium hydroxide, toluene, or xylene, photocyclization of **5**, **6** occur exclusively. The triplet state is mainly involved in the photocyclization of **5** or **6**, because of the inhibition of oxygen.

### INTRODUCTION

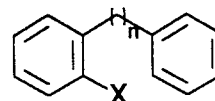
The intermolecular photochemical reaction of iodo-benzene in benzene to afford diphenyl has been known since 1961.<sup>1</sup> The related photochemical reactions of appropriately substituted haloarenes has been studied extensively.<sup>2</sup> These reactions are of considerable importance in organic syntheses and in degrading halogenated arenes which pollute the environment. We have been interested in the intramolecular photocyclization of N-(arylmethyl)-2-chloropyridinium salts,<sup>3</sup> N-[(2-haloaryl)methyl]pyridinium salts,<sup>4</sup> and 2-haloarenes.<sup>5</sup>

Here we report the photochemical reactions of 1-halo-2-(phenylalkyl)benzenes and the reaction mechanism. The substrates are several haloarenes in which both aryl ring and haloaryl ring are connected by alkyl groups (see Scheme 1). The photochemical reaction of 1-halo-2-(phenylalkyl)benzenes are presented here for the first time.

### MATERIALS AND METHODS

All melting points were determined on an Electro-thermal Melting Point Apparatus and are uncorrected. Nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were measured in CDCl<sub>3</sub> on Bruker AM-300, 300 MHz spectrometer. GC-mass spectra were determined on Hewlett Packard 5890 Series II. The photochemical reaction products were analyzed by FID detector in the gas chro-

matography with HP-1 capillary column (cross-linked 5% methyl silicon, 25 m). Ultraviolet absorption spectra were measured on Shimadzu, UV-265.



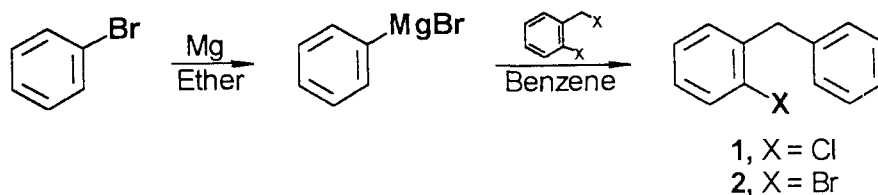
- 1**, n = 1, X = Cl  
**2**, n = 1, X = Br  
**5**, n = 2, X = Cl  
**6**, n = 2, X = Br

Scheme 1

#### Synthesis of 2-Benzyl-1-chlorobenzene (**1**)

A 500 mL three-necked flask, equipped with a sealed mechanical stirrer, a reflux condenser, and a pressure-equalized dropping funnel, was arranged for carrying out a reaction in an atmosphere of nitrogen by fitting into the top of the condenser a T-tube attached to a low pressure supply of nitrogen and a mercury bubbler. The 500 mL flask was dried by warming with a soft flame as a slow stream of nitrogen was passed through the system. A mixture of 7.3 g (0.3 atom) of magnesium turnings and 40 mL of ethyl ether was added into the 500 mL flask. To the flask, 20 mL of a mixture of 47 g (0.3 mol) of bromobenzene with 150 mL of ethyl ether were added. When starting the reaction, add 40 mL of ethyl ether and then add the rest of the mixture of bromobenzene slowly to insure boiling mildly. After adding the mixture, heat the mixture to reflux for 30 min. When the reaction is complete, the ether is replaced with dry benzene. This established a boiling point of 73°C for the mixture.

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Scheme 2

To the hot mixture, 22 g of 2-chlorobenzyl chloride in 100 mL benzene was added and then the mixture was heated to reflux for 1 hr. After cooling, 100 mL of 4 N HCl were added for the work-up. After separating the organic layer, wash it with water. After drying it with  $\text{CaCl}_2$ , distillate it under vacuum, b.p. 86–88°C (0.8 mmHg), yield 85%.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.08 (s,  $-\text{CH}_2-$ , 2H), 7.10–7.32 (m, Aromatic, 9H). MS:  $m/z$  204 ( $\text{M}^+ + 2$ ), 202 ( $\text{M}^+$ ), 167. The reaction path is shown in Scheme 2.

#### 2-Benzyl-1-bromobenzene (2)

The product was colorless oil (yield 78%). b.p.: 98–100°C/0.8 mmHg.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  4.07 (s,  $-\text{CH}_2-$ , 2H), 7.09–7.24 (m, Aromatic, 8H), 7.52 (d,  $J=7.9$  Hz, Aromatic, 1H). MS:  $m/z$  248 ( $\text{M}^+ + 2$ ), 246 ( $\text{M}^+$ ), 167.

#### 1-Chloro-2-phenethylbenzene (5)

The product was colorless oil (yield 81%). b.p.: 109–110°C/1.5 mmHg.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.82–2.85 (t,  $-\text{CH}_2-$ , 2H), 2.94–2.97 (t,  $-\text{CH}_2-$ , 2H), 6.99–7.25 (m, Aromatic, 9H). MS:  $m/z$  218 ( $\text{M}^+ + 2$ ), 216 ( $\text{M}^+$ ), 181.

#### 1-Bromo-2-phenethylbenzene (6)

The product was colorless oil (yield 74%). b.p.: 93–94°C/0.3 mmHg.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  2.86–2.89 (t,  $-\text{CH}_2-$ , 2H), 2.98–3.02 (t,  $-\text{CH}_2-$ , 2H), 6.97–7.23 (m, Aromatic, 8H), 7.48 (d, Aromatic, 1H). MS:  $m/z$  262 ( $\text{M}^+ + 2$ ), 260 ( $\text{M}^+$ ), 181.

Their synthetic procedures are the same as 1. The reaction paths are shown in Scheme 2, 3.

#### The Photochemical Reaction

The photochemical reaction of the haloarenes were accomplished in uv cuvette (5 mL, 2 cm path) using light pulse of Xe-lamp via solution filter (aqueous cobaltous sulfate solution).

The pertinent results are shown in Table 2 and 3.

#### Kinetic Study

The light intensities were determined using ferrioxalate actinometry. The light intensities which we used are summarized in Table 1. The quantum yields with  $\text{O}_2$  or without  $\text{O}_2$  were determined in the following method. An acetonitrile solution of 2 ( $1 \times 10^{-3}$  M, 3 mL) in UV cuvette was deaerated with argon or oxygen for 10 min. The solution in the cuvette was irradiated with Xe-lamp for several time intervals. The UV absorption at 299 nm was monitored and shown in Fig. 1.

The concentration change can be determined using  $\epsilon_{299}$  of fluorene ( $\lambda_{\text{max}}=299$  nm,  $\epsilon_{299}=8.9 \times 10^3$  L/mol cm)

The pertinent results are summarized in Table 2. The concentration change of 5 or 6 was monitored using the  $\epsilon_{297}=5.0 \times 10^3$  L/mol cm ( $\lambda_{\text{max}}$  of 8=297 nm, assuming the initial formation of the reaction is 9,10-dihydrophenanthrene).

Table 1. Light intensities at two wavelengths

Wavelength(nm)	Intensity(ein/sec)	Remark
259	$5.4 \times 10^{-9}$	Xe-lamp
264	$4.8 \times 10^{-9}$	Xe-lamp

## RESULTS

When the acetonitrile solution of bromobenzene 2 ( $1 \times 10^{-3}$  M, 4 mL) in quartz cell (5 mL) was irradiated with Xe-lamp for 2 hrs, 3 peaks (products) on gas chromatography were observed (see Fig. 2). Their retention times were 6.2, 8.0 and 13 min, respectively. The products of the retention time being 6.2 and 8.0 were separated and identified as diphenylmethane (3, 57% yield) and fluorene (4, 27% yield), respectively.

The singlet at 3.95 ppm and multiplet at 7.15–7.27 ppm in  $^1\text{H NMR}$  spectra of Fig. 3 are assigned to methylene protons and protons on phenyl rings of 3, respectively. The ratio of the singlet to multiplet is 1/5. The molecular ion peak at 168 ( $\text{M}^+$ , 100%) in the mass spectra of the product 3 is observed.

The  $^1\text{H NMR}$  spectra of the product of retention time being 8.0 min is shown in Fig. 4. The singlet at 3.88 ppm in  $^1\text{H NMR}$  spectra is assigned to methylene protons of fluorene 4. The multiplet at 7.28–7.36 ppm, and two doublets at 7.53 and 7.78 ppm are assigned to protons on the 2, 3, 6 and 7 carbons, and 1, 4 and 5, 8 carbons of 4, respectively. The molecular ion peak at 166 ( $\text{M}^+$ , 100%) in the mass spectra of the product 4 was observed. The rest peak of retention time being 13 min was not identified yet.

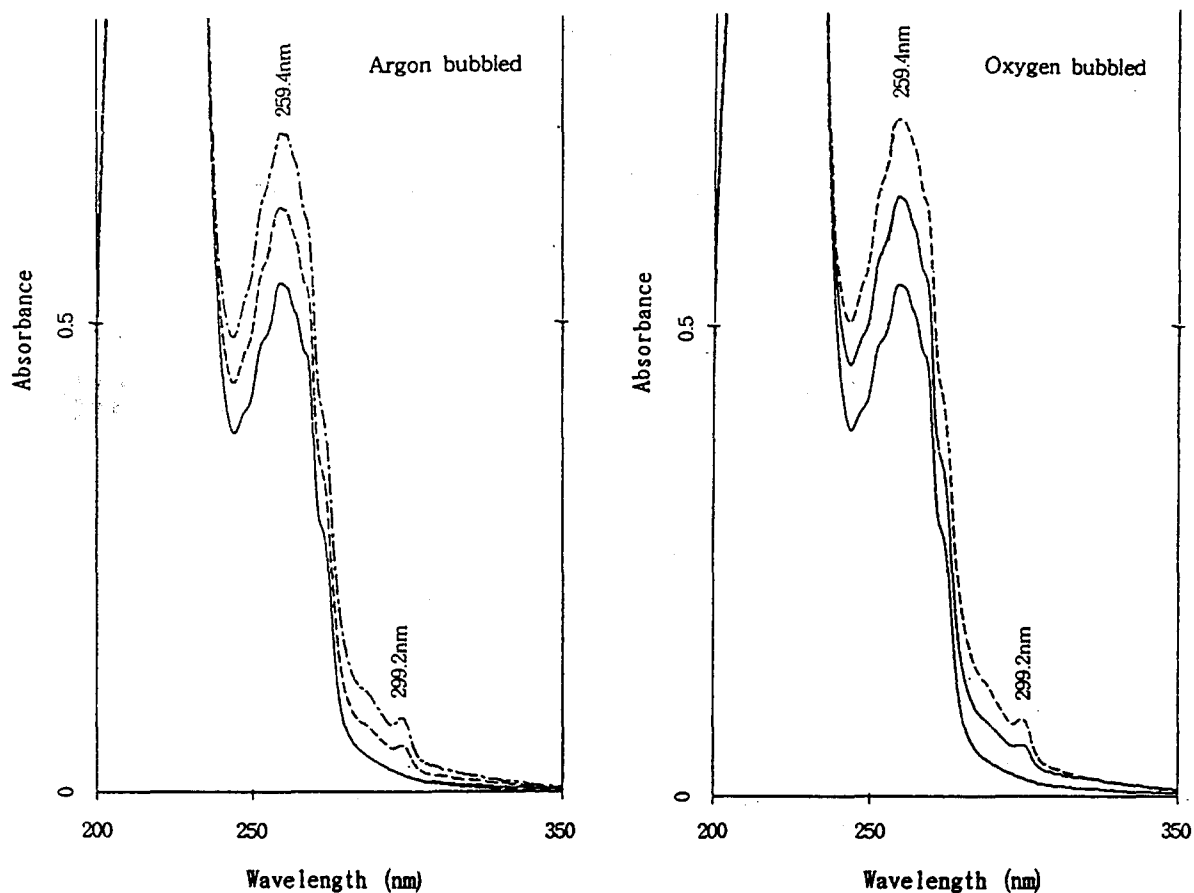


Figure 1. The change of absorption spectra of 2-benzyl-1-bromobenzene (2) in deaerated or aerated upon irradiation with Xe-lamp for 5 min or 10 min.

The yield of the photochemical reaction of halo-benzenes 1, 2 in several conditions are summarized in Table 2. The photoreduced product, diphenylmethane is major in acetonitrile or benzene solution

of 1 or 2. In cyclohexane able to donate a hydrogen atom, photoreduced reaction occurs exclusively. The introduction of a small amount of toluene or *p*-xylene ( $2 \times 10^{-3} M$ ) in acetonitrile solution caused

Table 2. The yields of photochemical reaction of 2-benzyl-1-halo-benzenes (1 or 2) in several conditions

Solvents	Reactants Products	1		2	
		3	4	3	4
Acetonitrile		57	18	57	27
Benzene		40	7	53	6
Cyclohexane		70	<1	55	8
AcCN+Toluene		38	33	67	23
AcCN+Xylene		9	53	35	57
AcCN+Et <sub>3</sub> N		86	4	89	3
AcCN+NaOH		41	53	9	76

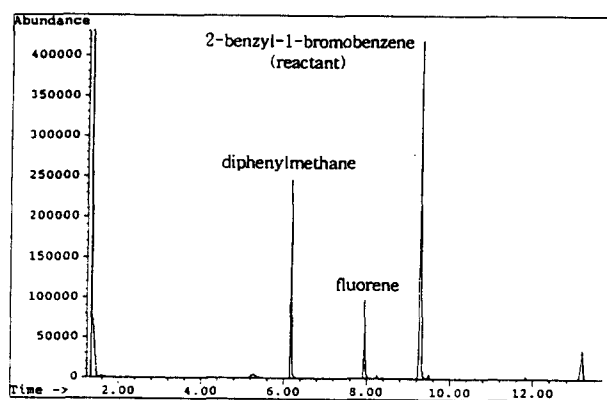


Figure 2. GC profile of crude photochemical reaction mixture of 2-benzyl-1-bromobenzene(2). The mixture was eluted with a linear gradient over 13 min of acetone.

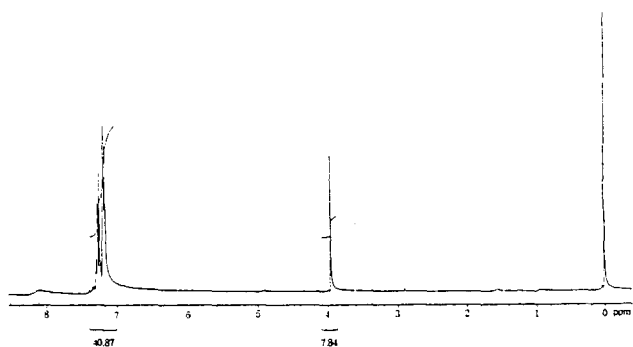


Figure 3.  $^1\text{H}$  NMR spectrum of the product of the retention time being 6.2 min [diphenylmethane (3)]

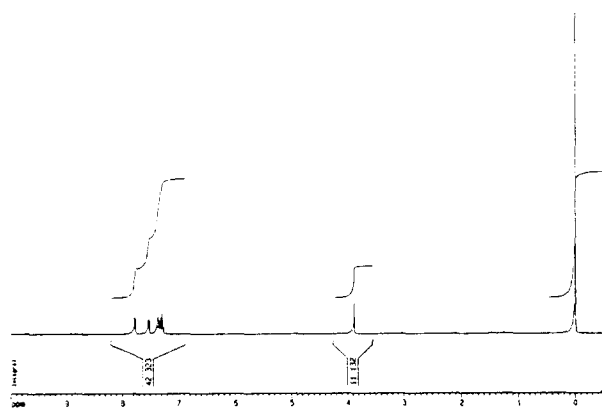


Figure 4.  $^1\text{H}$  NMR spectrum of the product of the retention time 8.0 min [fluorene (4)]

an increase in the amount of fluorene formed. The introduction of a small amount of triethylamine in acetonitrile caused an increase in the amount of diphenylmethane formed. The photocyclized product, fluorene is major in acetonitrile solution of **1** or **2** in the presence of sodium hydroxide.

When the acetonitrile solution of chlorophenethylbenzene **5** ( $1 \times 10^{-3}$  M, 4 mL) in the presence of p-xylene ( $2 \times 10^{-3}$  M) was irradiated by the above method, 6 peaks (products) on gas chromatography were observed (see Fig. 5). Their retention times were 7.2, 7.6, 9.2, 10.1 and 11.0 min. The products of retention time being 7.2, 9.21, and 10.1 were separated and identified as bibenzyl (7), 9,10-dihydrophenanthrene (8), and phenanthrene (9), respectively.

The singlet at 2.87 ppm and multiplet at 7.11-7.23 ppm in Fig. 6 are assigned benzyl protons and aromatic protons of **7**. The ratio of the singlet to multiplet is 2/5. The molecular ion peak at 182 ( $\text{M}^+$ , 28%) in the mass spectra is observed.

The singlet at 2.87 multiplet at 7.10-7.40 and

7.73 ppm are assigned to ethylene protons, aromatic protons, and protons of 4- and 5-carbons of **8**, respectively. The molecular ion peak at 180 ( $\text{M}^+$ , 100%) in the mass spectra of **8** is observed.

The multiplet at 7.60-7.72 ppm and two doublets at 7.87 and 8.67 ppm in  $^1\text{H}$  NMR of **9** are assigned to protons on 1, 2, 3, 6, 7 and 8 carbons, protons on 9 and 10 carbons, and protons on 4 and 5 carbons of **9**, respectively. The molecular ion peak at 178 ( $\text{M}^+$ , 100%) in the mass spectra of **9** is observed.

The yield of the photochemical reaction of halo-phenethylbenzenes **5** and **6** in several conditions are summarized in Table 3. 9,10-dihydrophenanthrene and phenanthrene are major products in the photochemical reaction of **5** or **6** in acetonitrile or benzene. The photoreduced product, bibenzyl is major in cyclohexane able to donate proton. The introduction of toluene or xylene ( $2 \times 10^{-3}$  M) to acetonitrile solution of **5** or **6** caused an increase in the amount of the photocyclized products (**8** + **9**) formed.

Introduction of triethylamine to the acetonitrile solution of **5** or **6**, caused an increase in the amount

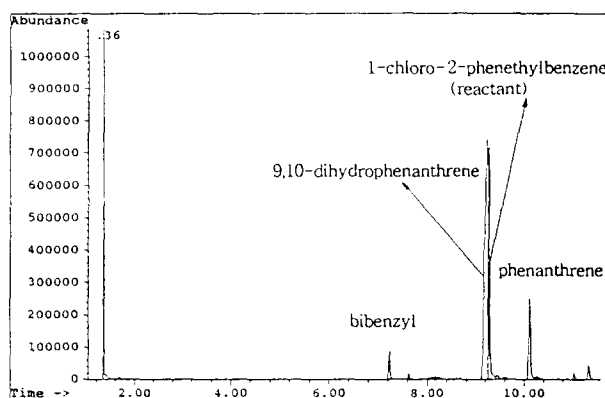


Figure 5. GC profile of crude photochemical reaction mixture of 1-chloro-2-phenethylbenzene (5)

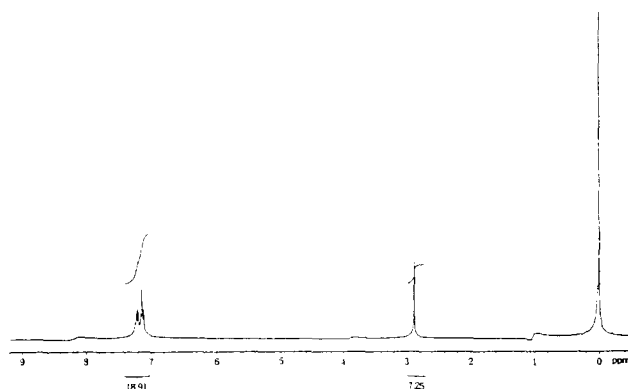


Figure 6.  $^1\text{H}$  NMR spectrum of the product of the retention time 7.2 min [bibenzyl (7)]

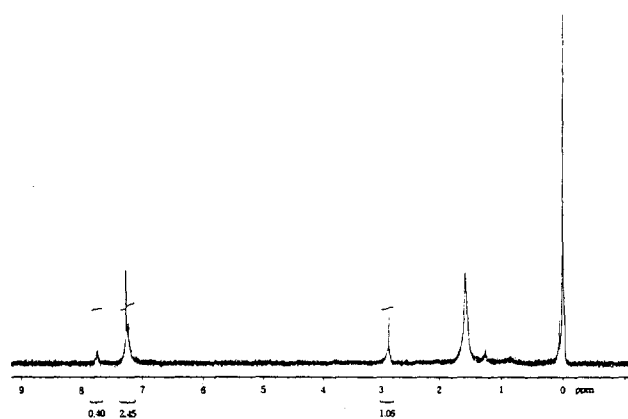


Figure 7.  $^1\text{H}$  NMR spectrum of the product of the retention time 9.2 min [9,10-dihydrophenanthrene (8)]

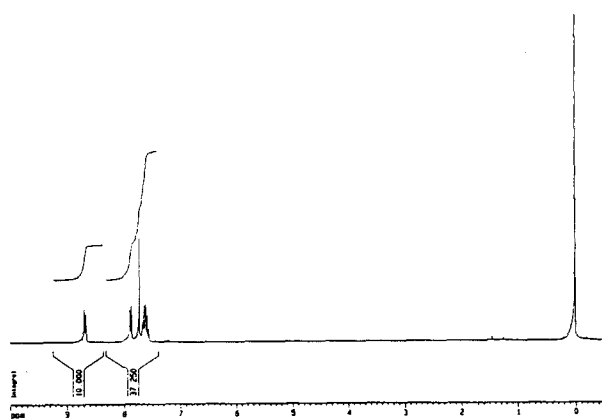


Figure 8.  $^1\text{H}$  NMR spectrum of the product of the retention time 10.1 min [phenanthrene (9)]

Table 3. The yields of photochemical reaction of 1-halo-2-phenethylbenzenes(5, 6) in several conditions

Solvents	Reactants Products	5		6	
		7	8+9	7	8+9
Acetonitrile		9	86	<1	75
Benzene		8	74	12	79
Cyclohexane		39	45	14	36
AcCN+Toluene		3	95	10	84
AcCN+Xylene		4	91	7	62
AcCN+Et <sub>3</sub> N		47	0	25	0
AcCN+NaOH		6	78	5	88

of 7, exclusively. The photocyclized products, 8, 9 are major in the presence of sodium hydroxide.

The quantum yield of the photocyclization of the aryl halides with or without oxygen are summarized in Table 4. The quantum yields in the table range

Table 4. Quantum yields in photocyclization of 1-halo-2-(phenylalkyl)benzenes(1, 2, 5, 6) in acetonitrile

Substrates	Conditions	
	Without O <sub>2</sub>	With O <sub>2</sub>
1	0.023	0.024
2	0.035	0.036
5	0.069	0.047
6	0.049	0.028

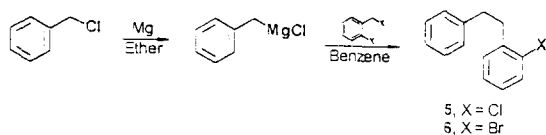
from a value of 0.023 for 1 to 0.069 for 5. The arene 5 in which the aryl ring and chloroarene ring are connected by ethylene group is, under anaerobic conditions, the most reactive substrate, followed by bromoarene 6. Both afford the six membered ring compound. The quantum yield of the photocyclization of 1 or 2 is not effected by the presence of oxygen. That of 5 or 6 is effected by the presence of oxygen. The reaction was retarded by the presence of oxygen.

## DISCUSSION

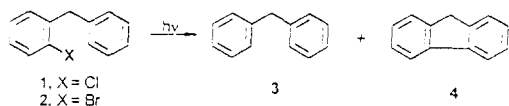
Chlorobenzene 1 is photoreduced to give diphenylmethane (3) in acetonitrile or benzene (see Table 2). In cyclohexane solvent able to donate hydrogen atom photoreduced reaction is exclusive. Haloarene 1 in acetonitrile with a small amount of toluene or xylene afford photocyclized product, fluorene (4), exclusively or increasingly. Probably toluene or xylene act as a hydrogen atom donor and a triplet sensitizer. The introduction of a small amount of triethylamine into acetonitrile solution of 1 affords a photoreduced product exclusively. Probably the reaction mechanism is different from the above reactions.

In the presence of alkali photocyclization reaction is exclusive or increased just like N-(2-chlorobenzyl) aniline.<sup>6,7</sup> The reaction pattern of 2-benzyl-1-bromobenzene (2) is the same as 1 above.

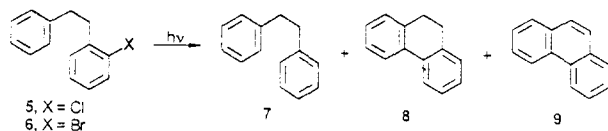
Chlorophenethylbenzene 5 is photocyclized to afford 9,10-dihydrophenanthrene (8) and phenanthrene (9) in acetonitrile or benzene (see Table 3). While the haloarenes 1 or 2 in which halophenyl and phenyl rings are connected by methylene is photoreduced, the other haloarene 5 or 6 in which halophenyl and phenyl rings are connected by ethylene is photocyclized in acetonitrile or benzene. Probably the two rings of the haloarene connected by ethylene could approach easily for the photocyclization. However, the rings of the haloarene connected by methylene could not approach easily for the photocyclization.



Scheme 3



Scheme 4



Scheme 5

In cyclohexane able to donate hydrogen atom the haloarenes **5** or **6** are photoreduced to afford bi-benzyl (**7**) increasingly just like **1** or **2**. In the presence of toluene, xylene, or sodium hydroxide in acetonitrile solvent, photocyclization of **5** or **6** occur exclusively. The photocyclization of **5** or **6** is effected by the presence of oxygen in acetonitrile. This indicates that the triplet state of **5**, **6** mainly is involved in the reaction. The photocyclization of **1** or **2** is not effected by the presence of oxygen. This indicates that the singlet state of **1** or **2** is involved for the cyclization portion of the photochemical reaction. The important result is that the quantum yield of photocyclization of chloroarene **5** is better than bromoarene **6**, even though the aryl-Cl bond is

stronger than the aryl-Br bond. There must be an assistance for the cleavage of the aryl-Cl bond via  $\pi$ -complex. The similar explanation is offered in N-(2-chlorobenzyl)pyridinium salt<sup>4,8</sup> and N-(2-chlorobenzyl)aniline.<sup>7</sup>

Thus we propose the reaction mechanism in Scheme 6. The singlet states are populated by light absorption of the haloarenes. The singlet states undergo either a cleavage of aryl-halogen bond to afford phenyl and halogen radicals, or a triplet state by the intersystem crossing process competitively. The phenyl radical also undergoes either photocyclization to give a conjugated hexadienyl derivative radical or photoreduction by abstraction of hydrogen atom from solvent or neighboring hydrogen donor. The hexadienyl radical could be formed from the triplet state too via  $\pi$ -complex. The hexadienyl radical can afford the cyclized product by losing the hydrogen atom.

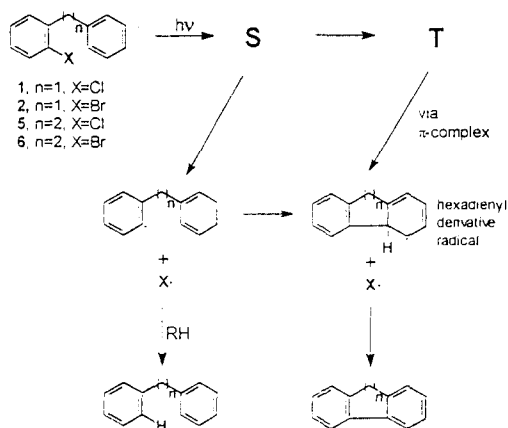
Toluene and xylene sensitize the haloarene to give the triplet of the haloarene by transferring the triplet energy to the haloarene and in turn produced more cyclized product.

We suppose that the singlet state is involved in the photoreduced reaction of the haloarene because of the inertness of the presence of oxygen. We are exploring the mechanism of the photoreduced reaction of the haloarene and will report on them in due course.

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Scheme 6

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