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The Photochemical Reactivities of Benzenes Tethered to Haloarene

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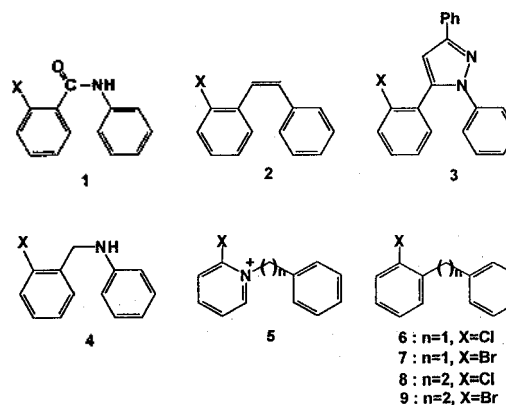*Department of Chemistry, Dong-A University, Pusan 604-714, Korea*
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The syntheses and photoreactions of haloarenes, in which the aryl and haloaryl moieties are tethered by a simple alkyl group, were studied. For 2-benzyl-1-halobenzene, in which two aryl moieties were connected by methylene group, photoreduced product, diphenylmethane, was obtained along with the minor formation of the photocyclized product, fluorene, in acetonitrile solvent. For 1-halo-2-phenethylbenzene, in which two aryl moieties were connected by ethylene group, photocyclized products, 9,10-dihydrophenanthrene and phenanthrene, were obtained along with the minor formation of photoreduced product, bibenzyl, in acetonitrile solvent. The photoreaction selectivities in several solvent systems were studied: In cyclohexane, 2-benzyl-1-chlorobenzene was photoreduced more effective than 2-benzyl-1-bromobenzene; In the presence of NaOH, 1-halo-2-phenethylbenzenes gave 9,10-dihydrophenanthrene and, in the presence of toluene, they gave phenanthrene. A radical reaction mechanism is proposed for the explanation of the reactions. This study shows that the photoreaction of haloarene, in which haloaryl and aryl moieties are tethered by ethylene group, can be used for ring formation of 9,10-dihydrophenanthrene otherwise difficultly accessible.

Introduction

Photoreactions of haloarenes are of considerable interest in the development of synthetic methods and in the understanding mechanistic pathways. The reactions are of interest for the degradation of the haloarenes which can pollute the environment. Intramolecular photocyclization of haloarenes, in which phenyl and 2-halophenyl moieties are linked by amide[1~3] (1), alkenyl[4,5] (2), 1,6-pyrazole[6] (3), and aminoalkyl groups[7~9] (4) have been studied (Scheme 1). Intramolecular photocyclization of halogenated pyridinium salts (5) also have been studied intensively.[10~13] However, little is known about the photoreactions of haloarenes in which the aryl and haloaryl moieties are connected by the simple alkyl groups (6-9). The photochemistry of these systems deserves special attention as should be the standard for the intramolecular photocyclization.

We now wish to report the first studies of the photoreactions and selectivities of the 1-halo-2-benzylbenzenes (6 or 7) and 2-halo-1-phenethylbenzenes (8 or 9).

Scheme 1.

Results and Discussion

Synthesis. 2-Benzyl-1-chlorobenzene (6) was prepared

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Table 1. The Yields of Photoreaction Products of 1-Halobenzyl-benzenes (6, 7) in Several Conditions

6, X=Cl
7, X=Br
10
11
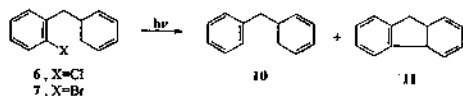
Haloarene	Solvent	Conv. (%)	Red. (%) (10)	Cyc. (%) (11)	Cyc./Red. (11/10)
6	Acetonitrile(AN)	55.6	39.6	31.3	0.8
	Benzene	84.9	26.5	3.8	0.1
	Cyclohexane	98.3	66.4	0.0	0.0
	AN + Et₃Nᵃ	52.4	54.6	28.8	0.5
	AN + Tolueneᵇ	53.1	41.1	31.6	0.8
	AN + Xyleneᶜ	59.6	32.4	25.5	0.8
	AN + NaOHᵈ	36.5	41.4	41.9	1.0
7	Acetonitrile(AN)	65.0	35.4	10.2	0.3
	Benzene	85.4	71.5	6.3	0.1
	Cyclohexane	44.6	24.7	5.4	0.2
	AN + Et₃Nᵃ	82.7	84.5	4.2	0.0
	AN + Tolueneᵇ	68.6	50.4	12.8	0.3
	AN + Xyleneᶜ	59.2	61.5	23.5	0.4
	AN + NaOHᵈ	66.1	41.8	18.5	0.4

ᵃ added 1.11 μL of triethylamine (4.0×10^{-3} M). ᵇ added 1.28 μL of toluene (6.0×10^{-3} M). ᶜ added 1.55 μL of xylene (6.0×10^{-3} M). ᵈ added 6.0×10^{-3} M NaOH in AN : H₂O (99 : 1)

by reacting 2-chlorobenzyl bromide with phenyl magnesium bromide. 2-Benzyl-1-chlorobenzene (6) was identified by nmr and mass spectra. 2-Benzyl-1-bromobenzene (7) was prepared by reacting 2-bromobenzyl bromide with phenyl magnesium bromide. The haloarene, 1-chloro-2-phenethylbenzene (8) and 1-bromo-2-phenethylbenzene (9) were also prepared by reacting the appropriate 2-halobenzyl bromide with benzyl magnesium bromide. The identification of the haloarene will be described in Experimental Section.

Preparative photoreaction. When the acetonitrile solution of 6 (5.0×10^{-3} M, 500 mL) in quartz immersion vessel was irradiated with Hg-lamp, two products, diphenylmethane (10) and fluorene (11), were isolated by preparative TLC in 46.6 and 20.8% yield, respectively. With reactant 7 the same products were obtained in 53.1 and 16.9% yield, respectively. The reactions are shown in the Table 1. For 6 or 7, the photoreduction reaction predominates with minor formation of photocyclized products. Presumably the first formed phenyl radical from the photolysis of 6 or 7 is not easily accessible to the other phenyl group within the molecule.

When the acetonitrile solution of 8 was irradiated as above, three products, bibenzyl (12), 9,10-dihydrophenanthrene (13), and phenanthrene (14), were isolated by preparative TLC in 4.8, 17.2, and 42.1% yield, respectively. The reactions are shown in the Table 2. With 9 the same products were obtained in 6.0, 1.0 and 60.0% yields respectively, under the above conditions. For 8 or 9, in which both aryl moieties are connected by ethylene group, photocyclization reactions predominate with minor formation of the photoreduced product. In this case the ethylene group allows the interacting

moieties are brought into sufficiently close proximity for the cyclization to occur. Other explanation is that ethylene connector permits more effective intramolecular exciplex than methylene one in the first excited state, although it needs further studies. Studies aimed at explaining the results more accurately are in progress. The yield of the photocyclization of >42% gives the reaction preparative value because the syntheses of 9,10-dihydrophenanthrene are otherwise difficult.

Photoselectivity. In order to study the photoreaction selectivities quantitatively, a simple reaction system was designed. An acetonitrile solution of 6 (2.0×10^{-3} M, 2 mL) was placed in ultraviolet cuvette, deaerated with argon gas, and then irradiated with light of wavelength 260 nm [with Xe-lamp(450 W)] for 2 hrs. The reactant conversion percentage and product yields were determined by GC with standard plots of the authentic materials. The pertinent results for 6 and 7 under several conditions are summarized in Table 1.

The photoreactions of both 6 and 7 were similar as indicated to the preparative scale study: the photoreduced product was major in most cases, except for 6 in acetonitrile in the presence of NaOH. Compared with 7 or 8, the less accessible conformation of 6 or 7 for aryl groups in proxmity to each other led mainly to photoreduced product in lieu of photocyclized product. In acetonitrile a moderate amount of photocyclized product (31.3%) was obtained for 6, while for 7 only 10.2% was obtained, although the photoreduced product was still major for both haloarenes. The ratios of cyclization to reduction for 6 and 7 were 0.8 and 0.3, respectively. The difference indicates the reaction selectivity: the chloroarene 6 gave more cyclized product than the bromoarene 7. The chlorine radical formed from homolytic cleavage of 6 could abstract a hydrogen of acetonitrile and the phenyl radical formed in acetonitrile cage, is close to the neighbor phenyl group to be cyclized. However, bromine radical from 7 could not easily abstract hydrogen of acetonitrile, but could only abstract benzyl hydrogen of the reactant itself and/or react with the phenyl radical to produce the reactant.

In benzene, both were photoreduced exclusively somehow. Presumably benzene molecules encumber the intramolecular photocyclization by forming a hydrophobic bonding with the phenyl moieties of 6 or 7. In cyclohexane, which is able to donate a hydrogen atom, photoreduction was exclusive for 6 (66.4%). However, this was not the case for 7, probably because bromine radical formed in homolytic cleavage of 7 by light absorption could not abstract hydrogen atom from cyclohexane effectively. The bond formation energy of H-Br (87.5 kcal/mol) was not enough for bond-breaking C-H (98 kcal/mol) in cyclohexane, while that of H-Cl (103.2 kcal/mol) was sufficient for breaking C-H in cyclohexane. In other words, back reaction to the starting material from halogen radical and phenyl type radical in the solvent cage for 7 is important, comparing to that of 6. High (98.3%) and low conversion percentage (44.6%) of 6 and 7 for 2 hours, respectively, supported the above explanation.

The introduction of triethylamine (2 equivalent for starting material) in acetonitrile solution of 6 or 7 caused an increase in the amount of photoreduced product, exclusively for 7.

The introduction of toluene or xylene in acetonitrile solu-

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Table 2. The Yields of Photoreaction Products of 2-Halophenethylbenzenes (**8**, **9**) in Several Conditions

8, X=Cl
9, X=Br
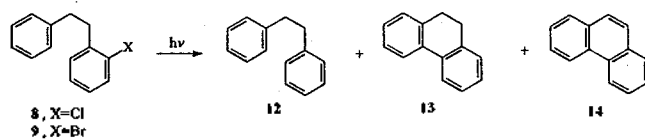
Haloarene	Solvent	Conversion (%)	Reduction (%) (12)	Cyclization (%)		Cyc./Red. (13+14/12)
				(13)	(14)	
8	Acetonitrile(AN)	24.4	9.0	52.5	0.7	7.0
	Benzene	83.2	7.0	49.5	8.1	8.2
	Cyclohexane	41.4	26.1	36.2	4.8	1.6
	AN+Et₃N[a]	70.2	7.3	18.7	0.0	2.5
	AN+Toluene[b]	79.4	2.5	66.5	19.5	34.4
	AN+Xylene[c]	88.9	1.7	53.3	12.7	38.8
	AN+NaOH[d]	65.0	1.8	55.2	1.2	31.3
9	Acetonitrile(AN)	50.9	6.3	3.3	61.3	10.3
	Benzene	60.6	16.0	73.8	0.0	4.6
	Cyclohexane	27.6	22.5	5.1	29.7	1.5
	AN+Et₃N[a]	80.7	16.5	14.5	0.0	0.9
	AN+Toluene[b]	46.5	9.2	10.5	45.6	6.1
	AN+Xylene[c]	47.9	11.7	45.9	41.7	7.5
	AN+NaOH[d]	34.2	11.4	66.7	0.0	5.8

[a] added 1.11 μL of triethylamine (4.0×10⁻³ M). [b] added 1.28 μL of toluene (6.0×10⁻³ M). [c] added 1.55 μL of xylene (6.0×10⁻³ M). [d] added 6.0×10⁻³ M NaOH in AN:H₂O (99:1)

tion of **6** did not change in the yields of products compared to that in acetonitrile only. However for **7**, the introduction caused an increase in the amount of photoreduced product, probably because toluene or xylene was a better hydrogen atom donor for the bromine radical formed.

In the presence of sodium hydroxide, photocyclization reaction was important for **6**. The similar behavior was also reported for photoreaction of N-(2-chlorobenzy)aniline (**4**) in the presence of NaOH.[9]

The conversion percentage and product yield for **8** and **9** were determined as above **6** and **7**, and summarized in Table 2.

For **8** and **9**, photocyclized products (**13**, **14**) were major in most solvents used. The ratios of cyclization to reduction were all larger than 1 for **8** and **9**, except for **9** in acetonitrile in the presence of triethylamine. The accessible proximity of two aryl moieties connected by ethylene group led to the cyclized products. Other explanation is that two aryl moieties can form an intramolecular exciplex of the excited state in a solvent cage.

Again for **8** and **9** in cyclohexane, the yields of photoreduced products increased compared to those in acetonitrile or benzene. Interestingly enough, phenanthrene, which formed from 9,10-dihydrophenanthrene, was major product in the reaction of **9**. Furthermore, the over-all reaction rate of **9** in cyclohexane is slower than any other ones in the conditions. These facts indicated that back reaction of bromine and phenyl radicals in solvent cage were important and the bromine radical abstracted only benzyl hydrogen of 9,10-dihydrophenanthrene.

In the presence of triethylamine, the yield of photocyclization for **8** and **9** diminished, probably the reaction mecha-

Table 3. Quantum Yields in Photocyclization of 1-Halo-2-(phenylalkyl)- benzenes (**6, 7, 8, 9**) in Acetonitrile

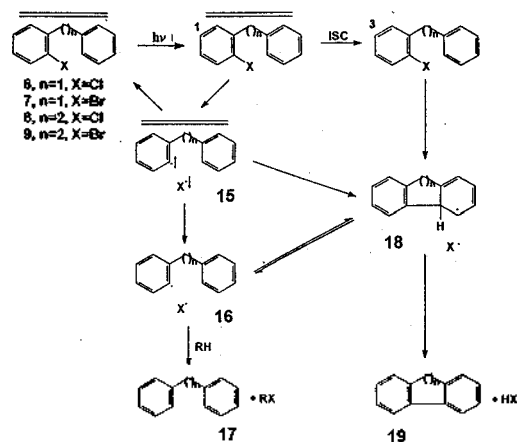| Conditions Haloarenes	Without O₂	With O₂
6	0.023	0.024
7	0.035	0.036
8	0.069	0.047
9	0.049	0.028

nism was different from the other reactions.

In the presence of toluene or xylene, the ratio of cyclization to reduction for **8** were great (34.4 and 38.8 for toluene and xylene, respectively), while that for **9** were moderate (6.1 and 7.5 for toluene and xylene, respectively). Toluene and xylene, presumably, sensitize the haloarenes to give the triplet state of the haloarenes (E_T: 83.0 and 84.9 kcal/mole for toluene and xylene).[14]

In the presence of sodium hydroxide, 9,10-dihydrophenanthrene was obtained in preference over phenanthrene.

The quantum yields of the photocyclization of the haloarene with or without oxygen are summarized in Table 3. The quantum yields in the table range from a value of 0.023 for **6** to 0.069 for **8**. The arene **8** in which the aryl ring and chloroarene rings are connected by ethylene group is, under anaerobic conditions, the most reactive substrate, followed by bromoarene **9**. The quantum yield of the photocyclization of **6** or **7** is not effected by the presence of oxygen. That of **8** or **9** is effected by the presence of oxygen. The reaction was retarded by the presence of oxygen. Thus, both

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Scheme 2.

singlet and triplet states of **8** and **9** are involved for the photocyclization, while the singlet states of **6** and **7** are involved for the photocyclization.

We propose a reasonable mechanism for the reaction in Scheme 2. The singlet state are populated in a solvent cage by light absorption of haloarenes. Some singlet states proceed to the triplet state by the intersystem crossing, while other singlet states undergo cleavage of aryl-halogen bond to afford a pair of phenyl and halogen radicals held together by a solvent cage. The strength of the cage depends upon solvent used. Most phenyl and halogen radicals within cage (**15**) return to the ground state, while other radicals either escape from the cage to give a free σ-phenyl and halogen radicals, or undergo reaction that cyclized product would be *via* cyclohexadienyl radical (**18**). The σ-phenyl radical can be reduced by abstraction of a hydrogen atom from a neighbor molecules. The cyclohexadienyl radical (**18**) can be formed from three ways: the triplet state, caged (**15**), and cage-free σ-phenyl radicals (**16**). The cyclohexadienyl radical (**18**) can afford the cyclized products by loosing a hydrogen atom. The σ-phenyl radical and halogen radical in a solvent cage, and the triplet state are invoked to explain the photoreactivities of the haloarenes.

Experimental

All melting and boiling points were determined on an Electrothermal Melting Point Apparatus and are uncorrected. Nuclear magnetic resonance (^{1}H NMR) spectra were measured in CDCl$_3$ on Brucker 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 chlomatograph with HP-1 capillary column (cross-linked 5% methyl silicon, 25 m). Ultraviolet absorption spectra were measured on Shimadzu, UV-265.

Synthesis of 2-Benzyl-1-chlorobenzene (6). 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 war-

ming 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 diethyl 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 diethyl ether were added. Starting the reaction, add 40 mL of diethyl 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.

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 was added for the work-up. After separating the organic layer, wash it with water. After drying it with CaCl$_2$, distillation of the mixture gave a colorless oil (85%); bp 86-88 °C (0.8 mmHg); ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.08 (s, -CH$_2$-, 2H), 7.10-7.32 (m, aromatic, 9H); IR (carbon tetrachloride): 3063, 3026, 2919, 1602, 1442, 1037, 746 cm^{-1}; UV (acetonitrile): λ_{max} 260 nm (600); MS: m/z 204 (M$^+$ +2), 202 (M$^+$), 167.

Anal. Calcd. for C$_{13}$H$_{11}$Cl: C, 77.04; H, 5.47. Found: C, 77.07; H, 5.30.

2-Benzyl-1-bromobenzene (7). The product was obtained as colorless oil (78%); bp 98-100 °C/0.8 mmHg; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.07 (s, -CH$_2$-, 2H), 7.09-7.24 (m, aromatic, 8H), 7.52 (d, J=7.9 Hz, aromatic, 1H); IR (carbon tetrachloride): 3061, 3029, 2914, 1602, 1436, 1026, 744 cm^{-1}; UV (acetonitrile): λ_{max} 260 nm (600); MS: m/z 248 (M$^+$ +2), 246 (M$^+$), 167.

Anal. Calcd. for C$_{13}$H$_{11}$Br: C, 63.18; H, 4.49. Found: C, 63.29; H, 4.59.

1-Chloro-2-phenethylbenzene (8). The product was obtained as colorless oil (81%); bp 109-110 °C/1.5 mmHg, ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.82-2.85 (t, -CH$_2$-, 2H), 2.94-2.97 (t, -CH$_2$-, 2H), 6.99-7.25 (m, aromatic, 9H); IR(carbon tetrachloride): 3063, 3026, 2931, 1602, 1444, 1051, 750 cm^{-1}; UV (acetonitrile): λ_{max} 260 nm (510); MS: m/z 218 (M$^+$ +2), 216 (M$^+$), 181.

Anal. Calcd. for C$_{14}$H$_{13}$Cl: C, 77.59; H, 6.05. Found: C, 77.68; H, 6.14.

1-Bromo-2-phenethylbenzene (9). The product was obtained as colorless oil (74%); bp 93-94 °C/0.3 mmHg; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.86-2.89 (t, -CH$_2$-, 2H), 2.98-3.02 (t, -CH$_2$-, 2H), 6.97-7.23 (m, aromatic, 8H), 7.48 (d, aromatic, 1H); IR (carbon tetrachloride): 3061, 3026, 2930, 1602, 1469, 1026, 750 cm^{-1}; UV (acetonitrile): λ_{max} 260 nm (510); MS: m/z 262 (M^1 +2), 260 (M$^+$), 181.

Anal. Calcd. for C$_{14}$H$_{13}$Br: C, 64.39; H, 5.02. Found: C, 64.48; H, 4.91.

Their synthetic procedures are the same as **6**.

Preparative Photochemical Reactions

The acetonitrile solution of the haloarene **6** (5.0×10^{-3} M, 450 mL), in quartz immersion vessel (500 mL) was irradiated with Hg-lamp (100 W, medium pressure) for 10 hrs. The reaction mixture was evaporated and analyzed with preparative TLC (Silica gel 60 F$_{254}$). The product of R_f values 0.77, 0.72, and 0.67 (developing solvent; petroleum ether : chloro-

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form = 30 : 1, V/V) were separated. The product of R_f 0.77 was identified as the starting material. The product of R_f 0.72 was identified as diphenylmethane with the following data: mp 25.5 °C; ^{1}H NMR: δ, 3.95 (s, 2H, C_{sp3}-H), 7.15-7.27 (m, 10H, aryl hydrogen); MS: (m/z) 168 (M[+]), 167 ($C_{13}H_{11}^+$), 91 ($C_7H_7^+$). The product of R_f 0.67 was identified as fluorene with the following data: mp 116-117 °C; ^{1}H NMR: δ, 3.88 (s, 2H, C_{sp3}-H), 7.28-7.36 (m, 4H, 2,3,6,7-H), 7.53 (d, 2H, 1,8-H), 7.78 (d, 2H, 4,5-H); MS: (m/z) 166 (M[+]), 165 (M[+]-H).

For **8**, the photochemical products which on R_f values of 0.81, 0.78, 0.75, and 0.71 were separated(developing solvent; petroleum ether : chloroform : triethylamine = 50 : 2 : 1, V/V). The product of R_f 0.81 was identified as the starting material. The product of R_f 0.75 was identified as 9,10-dihydrophenanthrene with the following data: mp 34 °C; ^{1}H NMR: δ, 2.73 (s, 4H, benzyl hydrogen), 7.00-7.47 (m, 6H, aryl hydrogen), 7.57-7.73 (m, 2H, 4,5-H); MS: (m/z) 180 (M[+]). The products being R_f 0.78 was identified as bibenzyl with the following data: mp 52 °C; ^{1}H NMR: δ, 2.87 (s, 4H, benzyl hydrogen), 7.11-7.23 (m, 10H, aryl hydrogen); MS: (m/z), 182 (M[+]), 91 ($C_7H_7^+$). The product being R_f 0.71 was identified as phenanthrene by comparing it with the authentic material.

Photoreaction Selectivity

An appropriate solvent solution of the haloarene (**6, 7, 8** or **9**, 2 mL, 2.0×10^{-3} M) was placed in 2.5 mL quartz cell, and then irradiated with Xe-lamp (450 W) via solution filter (aqueous cobalteous sulfate solution) for 2 hrs. The irradiated solution was analyzed using GC (sample injection 1 μL, injection temperature 220 °C, detector temperature 250 °C, ATT.10). The starting material and products were separated nicely on the GC. Their retention times were 6.21, 8.02, 8.41 min for **6**. The products of the retention time being 6.21, 8.02 and 8.41 were identified as diphenylmethane, fluorene and **7**, respectively by comparing with the authentic materials.

Oxygen effect on quantum yield. The light intensities were determined using ferrioxalate actinometry. The quantum yield with O_2 or without O_2 were determined as the following method. An acetonitrile solution of **7** (1×10^{-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. The concentration change can be determined using ε_{299} of fluorene ($\lambda_{max} = 299$ nm, $\varepsilon_{299} = 8.9 \times 10^3$ L/mol cm). The concentration change of **8** or **9** was monitored using the $\varepsilon_{297} = 5.0 \times 10^3$ L/mol cm (λ_{max} of **13** = 297 nm, assuming the initial formation of the reaction is 9,10-dihydrophenanthrene).

The perinent results are summarized in Table 3.

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