

Redox-Photosensitized Aminations of 1,2-Benzo-1,3-cycloalkadienes, Arylcyclopropanes, and Quadracyclane with Ammonia

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Received February 13, 2003

1,2,4-Triphenylbenzene and 2,2'-methylenedioxy-1,1'-binaphthalene successfully photosensitized the aminations of 1,2-benzo-1,3-cycloalkadienes, arylcyclopropanes, and quadracyclane with ammonia and primary amines in the presence of *m*- or *p*-dicyanobenzene, which gave the 4-amino-1,2-benzocycloalkenes, 3-amino-1-arylpropanes, and 7-amino-5-(*p*-cyanophenyl)bicyclo[2.2.1]hept-2-ene, respectively. A key pathway for the photosensitized amination is the hole transfer from the cation radicals of the sensitizers that were generated by photoinduced electron transfer to the electron acceptors to the substrates. Therefore, it was found that the relationships in oxidation potentials between the sensitizers and the substrates and the positive charge distribution of the cation radicals of the substrates were important factors for the efficient amination.

Introduction

The photochemical synthetic method has received much attention as an environmentally friendly synthetic process. We have developed the direct amination with ammonia by photoinduced electron transfer (*photoamination*) without using an acid or an alkaline.¹ So far, we have investigated the photoamination of a variety of arenes and aryl-substituted alkenes.² However, the photoamination has been restricted to the substrates that have a strong absorption near the UV region (>300 nm), since usual electron-transfer photosensitization by aromatic nitriles (e.g., 1-cyanonaphthalene,³ 1,4-dicyanonaphthalene,⁴ 9,10-dicyanoanthracene⁵) could not be applied to the photoamination due to the quenching of

these sensitizers by ammonia and amines. Redox photosensitization is a powerful method for achieving efficient reactions via photoinduced electron transfer.⁶ Recently, redox photosensitization by 2,2'-methylenedioxy-1,1'-binaphthalene (BN) and its derivatives has been successfully applied to the photoamination of 1,2-diarylcyclopropanes.⁷ Here, we will extensively apply redox photosensitization by BN and polyphenylbenzenes to the amination of 1,2-benzo-1,3-cycloalkadienes (**1a–d**), arylcyclopropanes (**3a–e**),⁸ and quadracyclane (**3f**), which have a weak absorption at >300 nm.

Results and Discussion

Redox Photosensitizer. Previously, it has been reported that the additions of alcohols and water to indene (**1a**) have been achieved by the electron-transfer photosensitization with 1-cyanonaphthalene (CNN).⁹ In

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TABLE 1. Redox-Photosensitized Aminations of **1a–d** and **3a–f** with Ammonia and Alkylamines^a

entry	substrate	RNH ₂	DCB	ArH	product yield (%)	conversion (%)		recovery (%)	
						substrate	DCB	ArH	
1 ^b	1a	NH ₃	<i>m</i> -DCB	none	2a (5)	54	61		
2	1a	NH ₃	<i>m</i> -DCB	1,2,4-TPB	2a (79)	99	90	83	
3	1a	NH ₃	<i>m</i> -DCB	1,3,5-TPB	2a (12)	54	83	30	
4	1a	NH ₃	<i>m</i> -DCB	<i>p</i> -TB	2a (76)	99	72	66	
5	1a	NH ₃	<i>m</i> -DCB	<i>m</i> -TB	2a (34)	88	88	47	
6 ^c	1b	NH ₃	<i>m</i> -DCB	none	2b (31)	84	92		
7	1b	NH ₃	<i>m</i> -DCB	BN	2b (58)	100	70	22	
8	1b	NH ₃	<i>m</i> -DCB	1,2,4-TPB	2b (83)	92	77	92	
9 ^c	1c	NH ₃	<i>m</i> -DCB	none	2c (16)	93	98		
10	1c	NH ₃	<i>m</i> -DCB	1,2,4-TPB	2c (63)	97	96	92	
11 ^c	1d	NH ₃	<i>m</i> -DCB	none	2d (31)	89	100		
12	1d	NH ₃	<i>m</i> -DCB	1,2,4-TPB	2d (57)	98	100	94	
13	1a	<i>i</i> -PrNH ₂	<i>m</i> -DCB	1,2,4-TPB	2e (52)	77	87	96	
14	1a	<i>t</i> -BuNH ₂	<i>m</i> -DCB	1,2,4-TPB	2f (49)	66	85	92	
15 ^c	3a	NH ₃	<i>m</i> -DCB	none	4a (14)	17	85		
16	3a	NH ₃	<i>m</i> -DCB	BN	4a (40)	53	90	87	
17	3a	NH ₃	<i>m</i> -DCB	1,2,4-TPB	4a (71)	81	92	66	
18 ^c	3b	NH ₃	<i>m</i> -DCB	none	4b (27)	29	90		
19	3b	NH ₃	<i>m</i> -DCB	BN	4b (90)	100	76	45	
20	3b	NH ₃	<i>m</i> -DCB	1,2,4-TPB	4b (54)	100	58	78	
21 ^c	3c	NH ₃	<i>m</i> -DCB	none	4c (32), 4c' (9)	52	93		
22	3c	NH ₃	<i>m</i> -DCB	BN	4c (61), 4c' (18)	100	95	82	
23	3c	NH ₃	<i>m</i> -DCB	1,2,4-TPB	4c (49), 4c' (15)	100	80	82	
24	3d	NH ₃	<i>m</i> -DCB	1,2,4-TPB	no product ^d	65	97	78	
25 ^c	3e	NH ₃	<i>p</i> -DCB	none	5a (2)	54	50		
26	3e	NH ₃	<i>p</i> -DCB	BN	4e (4), 5a (40)	95	60	27	
27	3e	NH ₃	<i>p</i> -DCB	1,2,4-TPB	4e (8), 5a (49)	97	70	72	
28 ^c	3f	NH ₃	<i>p</i> -DCB	none	5b (0)	0	95		
39	3f	NH ₃	<i>p</i> -DCB	BN	5b (62)	85	38	70	
30	3f	NH ₃	<i>p</i> -DCB	1,2,4-TPB	5b (5)	20	50	62	

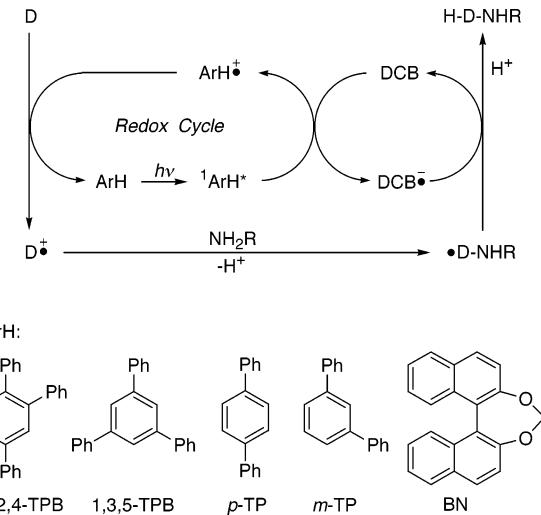
^a In the cases of the photoamination of **1a–d**, an MeCN–H₂O (19:1, 50 mL) solution containing **1** (2 mmol), DCB (3.75 mol), and ArH (0.75 mmol) was bubbled with ammonia and then irradiated for 5–13 h. In the cases of primary amines, an MeCN–H₂O (9:1, 50 mL) solution containing **1** (2 mmol), DCB (3.75 mol), and ArH (0.75 mmol) was bubbled with argon gas and then RNH₂ (20 mmol) was added and irradiated for 9 h (entries 13 and 14). In the cases of the photoamination of **3a–e**, the irradiation was performed for an ammonia-saturated MeCN–H₂O (9:1, 70 mL) solution containing **3** (3 mmol), DCB (3.5 mmol), ArH (1 mmol), and Et₄NBF₄ (7 mmol) for 20 h. The photoamination of **3f** was performed by the irradiation of an ammonia-saturated MeCN–H₂O (9:1, 70 mL) solution containing **3f** (3.5 mmol), DCB (3.5 mmol), and ArH (1 mmol) for 8 h. ^b Irradiation for an ammonia-saturated MeCN–H₂O (19:1; 50 mL) solution containing **1a** (27 mmol) and *m*-DCB (5 mmol). ^c Irradiation in the absence of ArH. ^d Aminated products were not formed.

a similar way, we attempted the CNN-photosensitized amination of **1a** with NH₃, but no photoamination occurred. Moreover, irradiation of an ammonia-saturated MeCN–H₂O (v/v, 9:1, 50 mL) containing **1a** (27 mmol) and *m*-dicyanobenzene (*m*-DCB, 5 mmol) for 52 h gave 2-aminoindan (**2a**, 5%) and a dimer of **1a** (18%) in low conversion (54%) (Table 1, entry 1). To improve the yield of **2a**, we intended to apply a redox photosensitization.

At first, we attempted to find arenes acting as a sensitizer, which are inert toward NH₃ and amines, because many arenes readily react with NH₃ under the conditions of the photoamination.^{2a} Recently, we have used 2,2'-methylenedioxy-1,1'-binaphthalene (BN) and the related compounds as redox photosensitizers for the photoamination of 1,2-diarylcyclopropanes.⁷ Although these sensitizers are inert toward NH₃ and amines, the BN-photosensitization would be restricted to substrates whose oxidation potentials were lower than that of BN ($E_{1/2}^{\text{ox}} = 1.20$ V). Indeed, the BN-photosensitized amination of **1a** ($E_{1/2}^{\text{ox}} = 1.33$ V) with NH₃ gave the colored solution from which a trace of **2a** and a large amount of **1a** (65%) were isolated.

We have previously found that polyphenylbenzenes have relatively high oxidation potentials and are inert toward NH₃ under the photoamination conditions.^{2d} However, many polyphenylbenzenes are poorly soluble

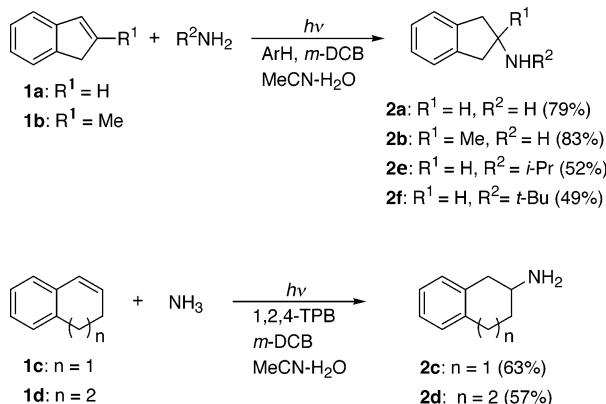
SCHEME 1. Redox Photosensitization



in aqueous MeCN solutions. As sensitizers that were moderately soluble in an aqueous MeCN solution, we therefore selected 1,2,4-triphenylbenzene (1,2,4-TPB), 1,3,5-triphenylbenzene (1,3,5-TPB), *m*-terphenyl (m-TP), and *p*-terphenyl (*p*-TP) (Scheme 1).

To find the more effective sensitizer among the above polyphenylbenzenes, the control experiments were per-

SCHEME 2

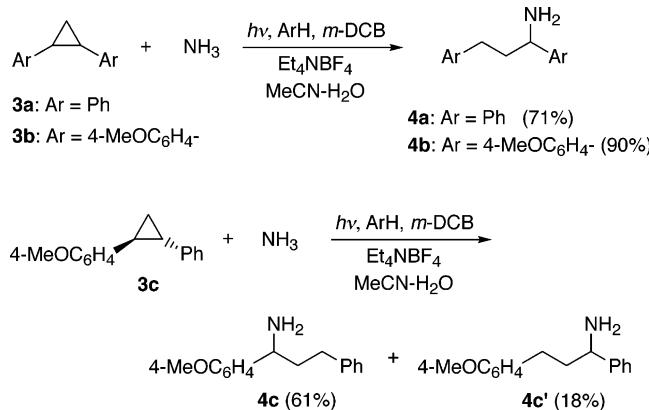


formed for the photoamination of **1a** with NH_3 (entries 2–5). Irradiation of an ammonia-saturated $\text{MeCN-H}_2\text{O}$ (19:1, 50 mL) solution containing **1a** (2 mmol), *m*-DCB (3.75 mmol), and the polyphenylbenzene (0.75 mmol) for 5–13 h gave **2a** (Scheme 2). When 1,2,4-TPB and *p*-TP were used as the sensitizer, the photoamination of **1a** proceeded in good yields (entries 2 and 4). However, *p*-TP was deposited during the irradiation because of the poor solubility in an $\text{MeCN-H}_2\text{O}$ solution. Therefore, we selected 1,2,4-TPB as the sensitizer for the photoamination. Moreover, the necessity of *m*-DCB was confirmed by the control experiment where no reaction occurred in the absence of *m*-DCB even upon prolonged irradiation.

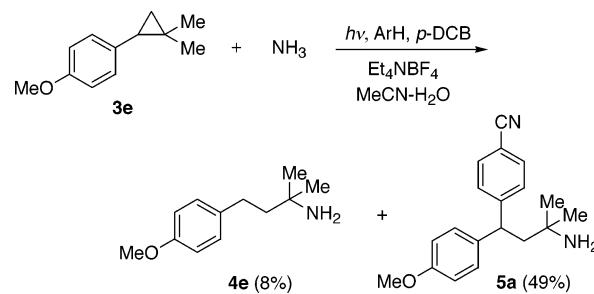
Redox-Photosensitized Amination. The 1,2,4-TPB-photosensitized amination of 2-methylindene (**1b**), 3,4-dihydronaphthalene (**1c**), and 1,2-benzo-1,3-cyclohepta-diene (**1d**) with NH_3 gave 2-amino-2-methylindan (**2b**), 2-amino-1,2,3,4-tetrahydronaphthalene (**2c**), and 4-amino-1,2-benzocycloheptene (**2d**), respectively, in high yields compared with the photoamination without sensitizers (entries 6–12). The 1,2,4-TPB-photosensitized aminations of **1a** with alkylamines, *i*-PrNH₂ and *t*-BuNH₂, were carried out by the irradiation of an $\text{MeCN-H}_2\text{O}$ solution (v/v, 19:1) containing **1a**, *m*-DCB, 1,2,4-TPB, and the amines to afford the corresponding 2-alkylaminoindan (**2e–f**) along with a small amount of 2-indanol (entries 13 and 14). However, the photoamination of **1a** with *t*-BuNH₂ in the absence of water proceeded to give **2f** in poor yield (12%). Scheme 2 summarizes the aminated products with the optimum yields.

The redox photosensitization was applied to the amination of arylcyclopropanes (**3a–e**). The amination of 1,2-diphenylcyclopropane (**3a**) photosensitized by a pair of 1,2,4-TPB and *m*-DCB gave 1-amino-1,3-diphenylpropane (**4a**) in high yield compared with the BN-photosensitization and the photoamination without the sensitizer (entries 15–17). Moreover, the direct irradiation of **3a** with NH_3 in the absence of *m*-DCB did not form **4a**, although it has been reported that the direct irradiation of **3a** with alkylamines (e.g., cyclohexylamine, piperidine, *n*-BuNH₂) gave the aminated products.¹⁰ When BN and 1,2,4-TPB were used as sensitizers, 1-amino-1,3-bis(*p*-methoxyphenyl)propane (**4b**) from the photoamination of *trans*-1,2-bis(*p*-methoxyphenyl)cyclopropane (**3b**) were obtained in 90 and 54% yields, respectively (entries

SCHEME 3



SCHEME 4

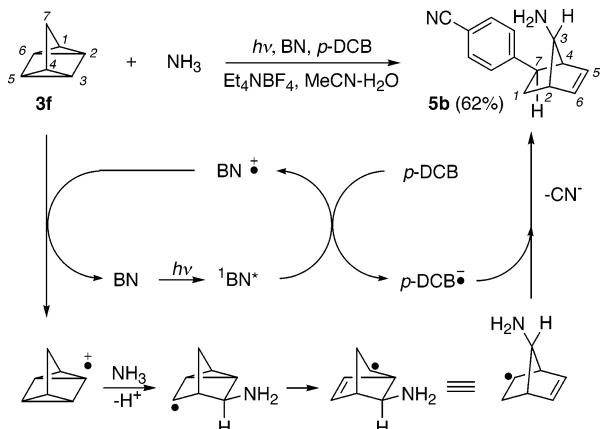


18–20). In the case of the photoamination of unsymmetric *trans*-1-(*p*-methoxyphenyl)-2-phenylcyclopropane (**3c**), 1-amino-1-(*p*-methoxyphenyl)-3-phenylpropane (**4c**) and its regioisomer (**4c'**) were formed (entries 21–23). However, *trans*-1-(2,4-dimethoxyphenyl)-2-phenylcyclopropane (**3d**) was not aminated (entry 24). In the photoamination of 1-(*p*-methoxyphenyl)-2,2-dimethylcyclopropane (**3e**) sensitized by a pair of BN and *p*-DCB or 1,2,4-TPB and *p*-DCB, the *p*-cyanophenyl group-incorporated aminated product, **5a**, was mainly obtained along with the formation of **4e**, while direct photoamination without the sensitizer gave **5a** in only 2% yield (entries 25–27). These aminated products from arylcyclopropanes (**3a–e**) are shown in Schemes 3 and 4 with the optimum yields. In cases of **3a–e**, the photoaminations were carried out in the presence of Et_4NBF_4 . Without Et_4NBF_4 , the yields of aminated products were decreased; for example, the yields of **4c** and **4c'** were 32%.⁷

The photosensitization by a pair of BN and *p*-DCB was effective for the amination of quadricyclane (**3f**) with NH_3 that gave 7-amino-5-(*p*-cyanophenyl)bicyclo[2.2.1]hept-2-ene (**5b**) in 62% yield (Scheme 5), while the photosensitization by a pair of 1,2,4-TPB and *p*-DCB was ineffective for the amination of **3f** (entries 28–30). The structure of the acetamide of **5b** was confirmed by X-ray crystallographic analysis.

Efficiency and Regiochemistry. From the comparison of absorption coefficients of **1a–d** ($\epsilon_{300} < 800 \text{ M}^{-1} \text{ cm}^{-1}$) and **3a–f** ($\epsilon_{300} < 300 \text{ M}^{-1} \text{ cm}^{-1}$) with those of the sensitizers (ArH) (Table 2), it was found that most of the incident light was absorbed by ArH under the reaction conditions. Therefore, the initiation step should be an electron transfer from the excited singlet states of ArH ($^1\text{ArH}^*$) to DCB, resulting in the cation radicals of ArH (ArH^+) and the anion radical of DCB. This mechanism

SCHEME 5



is confirmed from the following experiments: the fluorescences of ArH were quenched by DCB at nearly diffusion-controlled rates, and the free energy changes (ΔG) for the electron transfer were calculated to be negative or slightly positive by the Rehm–Weller equation (Table 2).¹¹ We have previously reported that the addition of salts such as Et_4NBF_4 and Et_4NOAc was effective in preventing back-electron transfer from DCB^- to substrates¹². Therefore, the addition of Et_4NBF_4 was effective in preventing the competitive back-electron transfer in the cases of **3a–e**.¹³

Moreover, the hole transfer from ArH^{+} to the substrates is a key pathway for the efficient photoamination. The efficiency of the hole transfer should depend on the difference in $E_{1/2}^{\text{ox}}$ between ArH and the substrates (Figure 1). In the case of the ArH -photosensitized amination of substrates whose $E_{1/2}^{\text{ox}}$ values were lower than those of ArH , efficient hole transfer would occur. However, the hole transfer did not occur from ArH^{+} to substrates whose $E_{1/2}^{\text{ox}}$ values were much higher than those of ArH . In the case of 1,2,4-TPB-photosensitized amination of **3f**, however, the yield of **5b** was very low (entry 30), although $E_{1/2}^{\text{ox}}$ of **3f** was much lower than that of 1,2,4-TPB. Because the hole transfer process from the cation radical of 1,2,4-TPB to **3f** is a much more exergonic process (0.89 eV = 85.9 kJ/mol), this process lies in the Marcus inverted region, resulting in slow hole transfer.¹⁴ In the case of 1,2,4-TPB-photosensitized amination of **3b**, **4b** was formed in 54% yield (entry 20), although the hole transfer of this reaction lies on Marcus inverted region. It is assumed that the nucleophilic attack of NH_3 occurred at the charge-transfer complex (1,2,4-TPB/**3b**)⁺ formed between the cation radical of 1,2,4-TPB and **3b**, which have a π -chromophore.^{2d,6,15}

The charge distribution of the resulting cation radicals of the substrates (**1** and **3**) is another factor determining

the efficiency of the photoamination. The charge distributions in the cation radicals of **1a–d** (**1a–d**⁺) and **3a–e** (**3a–e**⁺) were calculated by the ab initio method (Table 3). In **1a–d**⁺, the positive charge was distributed substantially over carbon C2 where the amination occurred actually. Dinnocenzo et al. has reported that the photo-induced nucleophilic addition of MeOH to the arylcyclopropanes proceeded via the nucleophilic attack on the cation radicals of the ring-closed cyclopropanes.¹⁶ We have also estimated that the photoamination of **3c** occurred by the nucleophilic attack on the ring-closed cation radical of **3c**, since the ab initio calculation of the ring-opened cation radical of **3c** showed that the positive charge developed over the benzylic carbon (+0.11) of the *p*-methoxyphenyl group but not over the benzylic carbon (−0.04) of the phenyl group where the photoamination actually occurred to give **4c'**. Therefore, the calculations of the charge distribution of **3a–e**⁺ were performed for the ring-closed cation radicals. The positive charge develops over the methoxy-substituted aryl group, except for the case of **3a**. In the case of **3d** having two methoxy groups, the positive charge localized more highly on the aryl group compared with the cases of the other cyclopropanes. This is one reason that the **3d**⁺ did not allow the nucleophilic attack of NH_3 to cyclopropane moiety, leading to no aminated products. Similar localization of the positive charge by the methoxy group has been previously observed in the cases of photoamination of stilbenes and styrenes having two or three methoxy groups, which underwent no amination to the olefinic moiety.^{2c,d}

As shown in Scheme 1, the nucleophilic addition of NH_3 at the ring-closed cation radicals of **3** gave the aminated radicals, which were reduced by DCB^- after the deprotonation and then followed by the protonation to give the aminated products (**4**). Therefore, the isomer ratio of **4** would depend on the relative stabilities of the aminated radicals ($\cdot\text{D-NHR}$ in Scheme 1).^{2g} The stabilities of the aminated radicals were estimated by the heats of the formations calculated by the ab initio method, as shown in Table 4. In the cases of the photoaminations of **1a–d**, the radicals **6A–9A** were much lower in energy than radicals **6B–9B**, as expected. In the case of **3e**, the radical **10A** was more stable than **10B** by ca. 127 kJ/mol. This result of the calculation was in agreement with the fact that the photoamination occurred selectively to give **4e** and **5a** via the **10A** intermediate. In the case of **3c**, on the other hand, the heats of the formations of the aminated radicals (**11A** and **11B**) were nearly equal to each other, thus giving a mixture of **4c** and **4c'**. Similarly, the photoaminations of **1a–d** proceeded according to Scheme 1, and the regioselectivities of **2a–d** were consistent with the stabilities of the aminated radicals, as shown in Table 4.

Roth et al. has reported the detailed product analysis for the *p*-DCB-photosensitized nucleophilic addition of MeOH to **3f**, which gave several types of the MeOH adducts.¹⁷ On the other hand, the present photoamination of **3f** gave **5b** as the sole product. Nucleophilic addition of NH_3 to **3f**⁺ might be faster than competitive side

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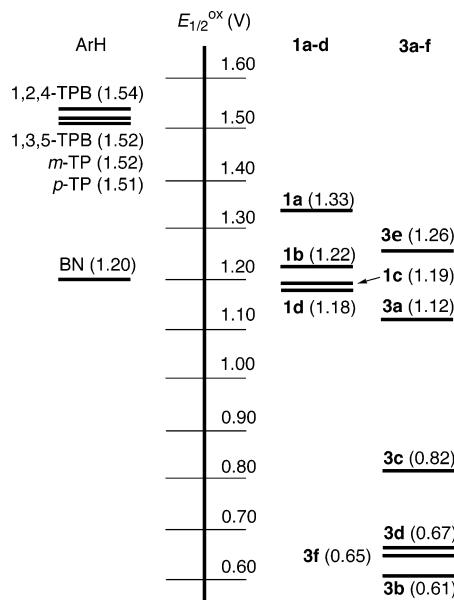
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TABLE 2. Properties of Sensitizers, Rate Constants for Fluorescence Quenching by DCB, and Calculated Free-Energy Changes^a

ArH	$E_{1/2}^{\text{red}}$ (V)	ϵ_{300} ($\text{M}^{-1}\text{cm}^{-1}$)	τ_F (ns)	E^{0-0} (kJ/mol)	K_{SV}^b (M^{-1})	k_q^c ($10^9 \text{ M}^{-1} \text{ s}^{-1}$)	ΔG^d (kJ/mol)
1,2,4-TPB	1.54	5160	2	369	28 (23)	14 (11)	-19 (-40)
1,3,5-TPB	1.52	830	42	346	108 (712)	2.6 (17)	+2 (-19)
<i>p</i> -TP	1.51	17 300	2	369	33 (25)	16 (12)	-22 (-43)
<i>m</i> -TP	1.52	2300	4	368	38 (41)	9.5 (12)	-20 (-41)
BN	1.20	12 000	2	303	26 (36)	13 (16)	14 (-7)

^a Values in parentheses are values for *p*-DCB. ^b Stern–Volmer constants for the fluorescence quenching of ArH by DCB. ^c Rate constant for the fluorescence quenching by DCB determined by fluorescence quenching. ^d Calculated by the Rehm–Weller equation using -1.93 and -2.15 V as $E_{1/2}^{\text{red}}$ of *p*-DCB and *m*-DCB, respectively.

**FIGURE 1.** Relationship between the oxidation potentials of **1a–d** and **3a–f** and those of ArH.**TABLE 3. Ab Initio Calculation^a on Charge Distribution on the Carbon Atoms in the Cation Radicals of **1a–d** and **3a–e^b****

1 and 3	group		reaction site	
	Ar	Ph	C1	C2
1a	+0.07		+0.01	+0.07
1b	0.00		0.00	+0.17
1c	+0.04		+0.01	+0.06
1d	+0.03		0.00	+0.06
3a	-0.18	-0.18	+0.06	+0.06
3b	+0.18	-0.13 ^c	-0.04	-0.08
3c	+0.23	-0.29	-0.08	-0.04
3d	+0.35	-0.28	-0.08	-0.04
3e	+0.11		-0.09	-0.03

^a Calculated by the ab initio method on SPALTAN program.

^b Calculation for the ring-closed cation radicals. ^c For the 4-MeOC₆H₄⁻ group.

reactions such as isomerization of **3f^{•+}** because of its strong nucleophilicity. Also, the rate of coupling of the aminated radical with the *p*-cyanophenyl anion radical was faster than that of the *p*-DCB-photosensitized addition of MeOH, probably because the redox photosensitization enhanced the concentration of the anion radical of *p*-DCB, thus providing efficient formation of **5b**.

Conclusion

Consequently, it was found that 1,2,4-TPB and BN were suitable sensitizers for the photoamination. These

TABLE 4. Difference in the Heat of Formation (ΔH) of the Aminated Radicals Calculated by the Ab Initio Method^a

favorable amino radicals	unfavorable amino radicals	ΔH (kJ mol ⁻¹)
		124.0
		111.5
		150.3
		12.5
		127.0
		5.3

^a Ab initio calculation was done on a Silicon Graphcs O2 workstation using the SPALTAN program.

sensitizers were able to sensitize substrates whose $E_{1/2}^{\text{ox}}$ values were ca. 0.06 V higher and ca. 0.9 V lower than those of the sensitizers. Thus, the redox-photosensitized amination provides a useful synthetic tool. For example, 2-aminoindan, an intermediate for synthesis of compounds with biological activities, was prepared by the direct photoamination of indene without special reagents such as acids and bases, whereas in general, it has been prepared from indene in four steps using several reagents.^{18,19} The present photoamination provides an environmentally friendly synthetic process to transform simple alkenes and cyclopropanes into the corresponding aminated compounds.

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Experimental Section

1,2,4-Triphenylbenzene (1,2,4-TPB). 1,2,4-TPB was prepared by the coupling reaction of 1,2,4-tribromobenzene (12.6 g) with PhMgBr in the presence of bis(triphenylphosphine)-nickel chloride (3 g) in Et₂O (150 mL): mp 100–101 °C (from MeOH, lit.²⁰ 99–100 °C); ¹H NMR δ = 7.14–7.20, (m, 9H), 7.31–7.50 (m, 5H), 7.61–7.68 (m, 4H); ¹³C NMR δ = 126.11, 126.50, 126.58, 127.12, 127.42, 127.89, 127.89, 128.81, 129.41, 129.85, 129.85, 131.09, 139.52, 140.34, 140.56, 140.95, 141.08, 141.45; MS *m/z* 306 (M⁺).

2,2'-Methylenedioxy-1,1'-binaphthalene (BN). The preparation of BN was performed by the reaction of (±)-2,2'-dihydroxy-1,1-binaphthalene (35 mmol) with dibromomethane (102 mmol) in the presence of K₂CO₃ (30 g) and NaI (0.5 g) in acetone (150 mL) at refluxing temperature for 40 h;²¹ mp 82.5–83.5 °C; ¹H NMR δ = 5.69 (s, 2H), 7.25–7.33 (m, 2H), 7.39–7.60 (m, 6H), 7.85–8.03 (m, 4H); ¹³C NMR δ = 103.12, 120.92, 124.97, 126.03, 126.89, 128.37, 130.30, 131.78, 132.15, 151.23; HRMS calcd for C₂₁H₁₄O₂ 298.1200, found 298.1014. Anal. Calcd for C₂₁H₁₄O₂: C, 84.54; H, 4.73; O, 10.73. Found: C, 84.37; H, 4.90; O, 10.73.

1,2-Benzo-1,3-cycloheptadiene (1d). The reaction of 1-benzosuberone (5.6 mmol) and *p*-toluenesulfonylhydrazide (8.1 mmol) in EtOH (180 mL) at refluxing temperature for 3 h gave a white precipitate, which was treated by butyllithium (in hexane 15%, 40 mL) in Et₂O (150 mL) at room temperature for 6 h (yield 65%): bp 61 °C (4 mmHg); IR (neat) 781 cm⁻¹ (lit.²² 782 cm⁻¹); ¹H NMR δ = 1.90–1.96 (m, 2H), 2.36–2.37 (m, 2H), 2.61 (t, *J* = 15.0 Hz, 2H), 5.63–5.91 (m, 1H), 6.39 (d, *J* = 10.0 Hz, 1H), 7.05–7.31 (m, 4H); ¹³C NMR δ = 26.90, 32.40, 36.05, 125.76, 126.46, 128.68, 129.77, 130.77, 132.09, 136.21, 141.56; HRMS calcd for C₁₁H₁₂ 144.0939, found 144.0947.

General Procedure of the Preparation of 1,2-Diaryl-cyclopropanes (3a–d). The reaction of the substituted benzaldehyde (100 mmol) with the substituted acetophenone (100 mmol) in the presence of KOH (2.0 g) in EtOH (100 mL) at room temperature gave the chalcone derivative.²³ The EtOH (50 mL) solution of the chalcone derivatives was refluxed with H₂N–NH₂/H₂O (12 mL) for 2 h, and then KOH (2.0 g) was added to the solution and heated at 200 °C for 2 h to give *cis*/trans mixtures of 3a–d. The trans isomers of 3b–d were isolated by column chromatography on silica gel. Compound 3a was used as a *cis/trans* mixture.¹⁰

trans-1,2-Bis(*p*-methoxyphenyl)cyclopropane (3b): mp 70.0–71.0 °C (lit.²⁴ 70.5–71.5 °C); ¹H NMR δ = 1.32 (t, *J* = 7.1 Hz, 2H), 2.04 (t, *J* = 7.1 Hz, 2H), 3.78 (s, 6H), 6.64 (d, *J* = 6.7 Hz, 4H), 7.07 (d, *J* = 6.7 Hz, 4H); ¹³C NMR δ = 17.35, 26.76, 55.31, 113.62, 126.62, 134.71, 157.76; HRMS calcd for C₁₇H₁₈O₂ 254.1305, found 254.1322.

trans-1-(*p*-Methoxyphenyl)-2-phenylcyclopropane (3c): mp 82.5–83.5 °C (lit.²³ 82.5–83.5 °C); ¹H NMR δ = 1.24–1.42 (m, 2H), 2.06–2.15 (m, 2H), 3.79 (s, 3H), 6.55–7.24 (m, 9H); ¹³C NMR δ = 17.79, 23.84, 27.49, 55.31, 113.63, 125.40, 125.66, 126.88, 134.49, 142.49, 142.71, 157.82; HRMS calcd for C₁₆H₁₆O 224.1200, found 224.1191.

trans-1-(2,4-Dimethoxyphenyl)-2-phenylcyclopropane (3d): mp 79.5–80.5 °C; ¹H NMR δ = 1.29–1.35 (m, 2H), 2.01–2.09 (m, 1H), 2.29–2.37 (m, 1H), 3.79 (s, 6H), 6.41–6.45 (m, 1H), 6.45 (s, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 7.12–7.31 (m, 5H); ¹³C NMR δ = 16.49, 21.46, 25.98, 55.39, 55.48, 98.50,

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103.94, 123.26, 125.48, 125.99, 126.11, 128.25, 143.21, 158.99, 159.16; HRMS calcd for C₁₇H₁₈O₂ 254.1307, found 254.1323. Anal. Calcd for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.07; H, 7.04.

1-(*p*-Methoxyphenyl)-2,2-dimethylcyclopropane (3e). 1-(*p*-Methoxyphenyl)-3-methyl-1-propene (3.24 g) in CHCl₃ (15 mL) was added to a CHCl₃ solution (30 mL) containing 50% aqueous NaOH solution (30 mL) and benzyltrimethylammonium chloride (40% in MeOH; 0.1 mL), and the reaction mixture was stirred for 1 day to give 1-(*p*-methoxyphenyl)-2,2-dichloro-3,3-dimethylcyclopropene in 95% yield.²³ The resulting product (0.3 g) was treated with Na (1.0 g) in Et₂O (50 mL) at room temperature for 1 day to give 3e: ¹H NMR δ = 0.70–0.73 (m, 2H), 0.77 (s, 3H), 1.97 (s, 3H), 1.80 (dd, *J* = 7.6, 6.6 Hz, 1H), 3.78 (s, 3H), 6.80 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H); ¹³C NMR δ = 18.37, 20.43, 27.31, 28.88, 55.16, 113.38, 129.87, 132.40, 152.56; HRMS calcd for C₁₂H₁₆O 176.1200, found 176.1234.

General Procedure of Photoamination. In the cases of **1a–d**, an ammonia-saturated MeCN–H₂O (19:1, 50 mL) solution of **1a–d** (2 mmol), DCB (3.75 mmol), and ArH (0.75 mmol) was poured into a Pyrex glass tube, sealed with a rubber septum, and irradiated with a high-pressure mercury lamp for 5–13 h at ambient temperature. In the cases of primary amines, an MeCN–H₂O (9:1, 50 mL) solution containing **1** (2 mmol), DCB (3.75 mmol), and ArH (0.75 mmol) was bubbled with argon gas, and then RNH₂ (20 mmol) was added and irradiated for 9 h. In the cases of **3a–e**, the irradiation was performed for an ammonia-saturated MeCN–H₂O (9:1, 70 mL) solution containing **3a–e** (3 mmol), DCB (3.5 mmol), ArH (1 mmol), and Et₄NBF₄ (7 mmol) for 20 h. In the case of **3f**, an MeCN–H₂O (9:1, 70 mL) solution containing *p*-DCB (3.5 mmol) and ArH (1 mmol) was bubbled with ammonia gas. After **3f** (3.5 mmol) was added, the solution was irradiated for 8 h.

After the irradiation, the photolysates were treated by Ac₂O. The starting materials, DCN, ArH, and the aminated products were separated by chromatography on silica gel. The formation of **2a** was confirmed by comparison with a commercially available authentic sample.

2-Amino-2-methylindan (2b): the acetamide; mp 54.0–56.0 °C; ¹H NMR δ = 1.55 (s, 3H), 1.92 (s, 3H), 3.00 (d, *J* = 15.8 Hz, 2H), 3.33 (d, *J* = 15.8 Hz, 2H), 5.61 (brs, 1H), 7.15–7.18 (m, 4H); ¹³C NMR δ = 24.29, 25.62, 46.18, 61.37, 124.75, 126.54, 141.30, 169.80; HRMS calcd for C₁₂H₁₅NO 189.1107, found 189.1152.

2-Amino-1,2,3,4-tetrahydronaphthalene (2c): the acetamide; mp 107.0–107.5 °C; ¹H NMR δ = 1.64–1.79 (m, 1H), 1.98 (s, 3H), 1.93–2.07 (m, 1H), 2.65 (dd, *J* = 16.2, 8.8 Hz, 1H), 2.80–2.85 (m, 2H), 3.04 (dd, *J* = 16.2, 5.1 Hz, 1H), 4.04–4.25 (m, 1H), 6.67 (brs, 1H), 6.96–7.13 (m, 4H); ¹³C NMR δ = 22.97, 27.22, 28.53, 35.27, 45.08, 125.41, 125.62, 128.34, 128.89, 133.91, 135.08, 169.52; HRMS calcd for C₁₂H₁₅NO 189.1154, found 189.1168. Anal. Calcd for C₁₂H₁₅NO: C, 76.16; H, 7.99; N, 7.40; O, 8.45. Found: C, 76.18; H, 8.00; N, 7.37; O, 8.45.

4-Amino-1,2-benzocycloheptene (2d): the acetamide; mp 146.5–148.0 °C; ¹H NMR δ = 1.60–1.69 (m, 2H), 1.80–2.02 (m, 2H), 1.87 (s, 3H), 2.74–2.78 (m, 2H), 2.90 (dd, *J* = 13.7, 8.2 Hz, 1H), 3.00 (dd, *J* = 13.7, 1.8 Hz, 1H), 4.05–4.17 (m, 1H), 5.76 (brd, *J* = 6.2 Hz, 1H), 7.07–7.15 (m, 4H); ¹³C NMR δ = 23.30, 24.40, 35.80, 37.20, 41.10, 46.80, 126.30, 126.90, 129.00, 129.30, 137.10, 143.20, 169.20; HRMS calcd for C₁₃H₁₇NO 203.1309, found 203.1354. Anal. Calcd for C₁₃H₁₇NO: C, 76.81; H, 8.43; N, 6.89; O, 7.87. Found: C, 76.61; H, 8.27; N, 6.85; O, 8.27.

2-Isopropylaminoindan (2e): the acetamide; mp 137.0–138.0 °C; ¹H NMR δ = 1.23 (d, *J* = 6.6 Hz, 6H) and 1.35 (d, *J* = 6.5 Hz, 6H), 2.11 (s, 3H) and 2.07 (s, 3H), 2.85 (dd, *J* = 14.9, 8.6 Hz, 2H) and 3.03–3.19 (m, 2H), 3.03–3.19 (m, 1H) and 3.86–4.07 (m, 1H), 3.70 (dd, *J* = 14.9, 9.9 Hz, 2H) and 3.86–4.07 (m, 2H), 3.86–4.07 (m, 1H) and 4.49–4.64 (m, 1H), 7.07–

7.18 (m, 8H); ^{13}C NMR δ = 21.00 and 20.24, 23.53 and 23.80, 36.13 and 37.25, 49.50 and 46.44, 53.31 and 56.71, 124.04 and 124.33, 125.74 and 126.65, 141.74 and 140.08, 169.17 and 169.17; HRMS calcd for $\text{C}_{14}\text{H}_{19}\text{NO}$ 217.1467, found 217.1439. Anal. Calcd for $\text{C}_{14}\text{H}_{19}\text{NO}$: C, 77.38; H, 8.81; N, 6.45; O, 7.36. Found: C, 77.48; H, 8.82; N, 6.42; O, 7.28.

2-*t*-Butylaminoindan (2f): the acetamide; mp 95.0–95.5 °C; ^1H NMR δ = 1.49 (s, 9H), 2.00 (s, 3H), 3.24 (d, J = 9.2 Hz, 4H), 2.63 (quint, J = 9.2 Hz, 1H), 7.13–7.25 (m, 4H); ^{13}C NMR δ = 26.50, 30.00, 39.90, 53.80, 58.30, 124.70, 126.70, 140.80, 172.40; HRMS calcd for $\text{C}_{15}\text{H}_{21}\text{NO}$ 231.1623, found 231.1659. Anal. Calcd for $\text{C}_{15}\text{H}_{21}\text{NO}$: C, 77.88; H, 9.15; N, 6.05; O, 6.92. Found: C, 77.79; H, 9.12; N, 6.07; O, 7.02.

1-Amino-1,3-diphenylpropane (4a): The structure was determined by comparison of ^1H and ^{13}C NMR spectra with the authentic sample prepared by reductive amination of 2-tetralone with NH_4OAc and NaBCN_3 .¹⁸ The acetamide; ^1H NMR δ = 1.89 (s, 3H), 2.03–2.15 (m, 2H), 2.53–2.63 (m, 2H), 5.00 (q, J = 7.7 Hz, 1H), 6.24 (brs, 1H), 7.10–7.33 (m, 10H); ^{13}C NMR δ = 23.27, 32.59, 37.68, 53.29, 125.80, 126.48, 127.22, 128.15, 128.26, 128.52, 141.26, 141.99, 169.15; HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{NO}$ 253.3471, found 253.3440.

1-Amino-1,3-bis(*p*-methoxyphenyl)propane (4b): the acetamide; ^1H NMR δ = 1.93 (s, 3H), 2.05–2.56 (m, 4H), 3.78 (m, 3H), 3.79 (m, 3H), 4.87–4.98 (m, 1H), 6.78–7.27 (m, 8H); ^{13}C NMR δ = 20.71, 31.54, 37.69, 52.69, 55.14, 113.74, 113.96, 127.72, 129.11, 133.36, 133.94, 158.72, 158.74, 169.71; HRMS calcd for $\text{C}_{19}\text{H}_{23}\text{NO}_3$ 313.1677, found 313.1677.

1-Amino-1-(*p*-methoxyphenyl)-3-phenylpropane (4c): the acetamide; ^1H NMR δ = 1.94 (s, 3H), 2.06–2.24 (m, 2H), 2.54–2.63 (m, 2H), 3.80 (s, 3H), 4.92–5.01 (m, 1H), 5.70 (d, J = 8.2 Hz, 1H), 6.86–6.89 (m, 3H), 7.13–7.32 (m, 6H); ^{13}C NMR δ = 22.92, 31.44, 37.84, 52.95, 54.95, 113.58, 126.37, 126.96, 128.31, 128.98, 133.23, 142.24, 157.54, 169.48; HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$ 283.1570, found 283.1541.

1-Amino-3-(*p*-methoxyphenyl)-1-phenylpropane (4c'): the acetamide; ^1H NMR δ = 1.94 (s, 3H), 2.06–2.24 (m, 2H), 2.54–2.63 (m, 2H), 3.80 (s, 3H), 4.92–5.01 (m, 1H), 5.70 (d, J = 8.2 Hz, 1H), 6.68–6.89 (m, 3H), 7.13–7.32 (m, 6H); ^{13}C NMR δ = 22.92, 32.41, 37.53, 52.44, 54.95, 113.69, 125.64, 127.55, 128.07, 128.13, 134.23, 141.27, 158.44, 169.36; HRMS calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$ 283.1570, found 283.1541.

3-Amino-1-(*p*-methoxyphenyl)-3-methylbutane (4e): the acetamide; ^1H NMR δ = 1.35 (s, 6H), 1.89 (s, 3H), 2.00 (t, J = 7.0 Hz, 2H), 2.51 (t, J = 7.0 Hz, 2H), 3.77 (s, 3H), 5.27 (brs, 1H), 6.81 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 8.6 Hz, 2H); ^{13}C NMR δ = 24.27, 26.99, 29.97, 41.81, 53.56, 55.13, 113.67, 129.14, 134.16, 157.59, 169.39; HRMS calcd for $\text{C}_{14}\text{H}_{21}\text{NO}_2$ 235.1567, found 235.1570.

3-Amino-1-(*p*-cyanophenyl)-1-(*p*-methoxyphenyl)-3-methylbutane (5a): the acetamide; ^1H NMR δ = 1.26 (s, 3H), 1.31 (s, 3H), 1.56 (s, 3H), 2.58 (d, J = 4.3 Hz, 2H), 3.74 (s, 3H); 4.06 (t, J = 4.3 Hz, 1H), 5.16 (brd, 1H), 6.83 (d, J = 8.7 Hz, 2H), 7.17 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 8.3 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H); ^{13}C NMR δ = 23.92, 27.76, 28.15, 43.50, 46.93, 53.53, 55.09, 109.46, 114.09, 116.80, 128.31, 128.58, 132.11, 135.71, 151.56, 158.14, 169.42; HRMS calcd for $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_2$ 336.1835, found 336.1804.

7-Amino-5-(*p*-cyanophenyl)bicyclo[2.2.1]hept-2-ene (5b): the acetamide; mp > 200 °C, ^1H NMR δ = 1.52 (s, 3H), 1.70–2.08 (m, 2H), 2.88–2.95 (m, 2H), 3.44 (d, J = 2.5 Hz, 1H), 3.75 (d, J = 7.5 Hz, 1H), 4.96 (brs, 1H), 6.18–6.29 (m, 2H), 7.45 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 7.5 Hz, 2H); ^{13}C NMR δ = 23.04, 30.46, 42.50, 44.41, 47.05, 64.23, 110.0, 119.0, 128.18, 132.04, 135.94, 136.04, 149.68, 170.0; HRMS calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}$ 252.1262, found 252.1203.

X-ray Crystallographic Analysis. X-ray crystallographic analysis was performed on an Enraf-Nonius CAD-4 system using Mo $\text{K}\alpha$ irradiation (λ = 0.71069 Å). All of the calculations were done on a DEC 3000 computer using the AXP Model 1300 program. Crystal data of the acetamide of **5b**: M = 250, monoclinic, Cc , a = 9.408 Å, b = 17.344 Å, c = 9.540 Å, β = 118.4°, V = 1369 Å³, Z = 4, D_m = 1.15 g/cm³, D_c = 1.22 g/cm³, R = 4.1%, R_w = 4.9%, number of unique reflections = 1790.

Supporting Information Available: ^1H and ^{13}C NMR spectra for new compounds (**2b**, **3e**, **4b**, **4c**, **4c'**, **4e**, **5a**) lacking combustion data and tables of X-ray data for the acetamide of **5b** involving the crystallographic parameters, positional parameters, bond distances, bond angles, and torsional angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO030053+