SYNTHETIC STUDY OF PHOTOINDUCED ELECTRON-TRANSFER REACTION LEADING TO REACTIONS OF CATION RADICALS WITH NUCLEOPHILES

（カチオンラジカル種と求核試剤との反応を誘起する光電子移動反応の合成化学的研究）

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Contents

General Introduction

Photoinduced electron-transfer reaction has received much attention as a convenient method for generation of ion radicals, thus offering a potentially useful procedure for chemical reactions. A large number of organic reactions induced by photoinduced electron transfer reaction between electron donor (D) and electron acceptor (A) have been developed, since ion radicals are very reactive species to undergo versatile organic reaction.[1] Especially, one of the particularly interesting reactions in this area is the addition of nucloephiles to electron-rich substrates (photoinduced nucleophilic addition). The photoinduced nucleophilic additions are induced by the formation of the cation radicals of D using photoinduced electron transfer.

Since first report of nucleophilic addition of methanol to 1,1-diphenylethene by Arnold et al in 1973,[2] the photoinduced nucleophilic additions to various substrates such as aryl-substituted alkenes, strain compounds, and arenes have been investigated using alcohols and water as nucleophiles.[3] However, little is known about the photoinduced nucleophilic addition of ammonia and amines. Moreover, the photoinduced nucleophilic additions of arenes have not been reported except for photocyanation,[4] because such weak nucleophiles as alcohols can not react with the arenes.[5] The photoaddition of ammonia and the amines is expected to show different features from that of other nucleophiles, since ammonia and the amines serve as both a nucleophile and a base. Therefore, the author has extensively studied the photoinduced nucleophilic addition of ammonia and amines to various aryl-substituted alkenes and arenes. If ammonia and amines can effectively add to the cation radicals of substrates, a useful synthetic procedure can be developed to achieve the direct amination of electron-rich substrates.

Also, great interest in photoinduced electron-transfer reactions has been paid to control of the outcome of these processes. The addition of salts is often effective to the controlling of photoreactions proceeding through exciplexs and ion radicals and brings about remarkable changes in reaction efficiencies.[6] On the other hand, a nucleophile is well known to interact

with cation radicals. Therefore, unusual effects of acetate ion having weak nucleophilicity to alter reaction courses have been investigated for electron-transfer photosensitized oxygenation of naphthalene and stilbene derivatives.

In order to develop new synthetic methology based on reaction of the cation radicals and nucleophiles, the author has investigated on photoinduced electron transfer according to the following four Chapters.

Chapter 1 deals with photoaddition of ammonia and alkylamines to aryl-substituted alkenes in the presence of dicyanobenzene to develop the highly efficient and selective reaction. The regiochemistry of the photoamination of unsymmetric 1-aryl-2-phenylethenes, and the improvement of the yield of the photoamintion of styrene derivatives will be discussed. Chapter 2 deals with direct photoamination of arenes with ammonia and primary amines in the presence of electron acceptor and stereochemistry of the photoamination. Chapter 3 deals with unusual effects of acetate ion on photosensitized oxygenation of naphthalene and stilbene derivatives via electron transfer. Chapter 4 deals with synthetic applications of photoinduced electron transfer to direct phosphonation of naphthalene and phenanthrene with trialkyl phosphites and to a synthesis of 1-amino-2-tetralone having medicinal interests by photoamination of 2-alkoxynaphthalenes with alkylamines.

References

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5) F. D. Lewis, *Adv. Photochem.*, **13**, 4404 (1986)

6) C. Pac and O. Ishitani, *Photochem. Photobiol.*, **48**, 767 (1988).

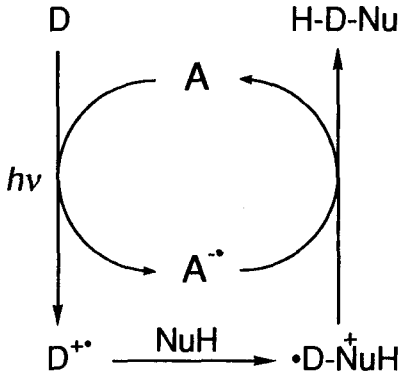
Chapter 1

Photoinduced Nucleophilic Addition to Aryl-Substituted Alkenes via Electron Transfer

1-1 Photoamination of 1,1-Diarylalkenes with Ammonia and Alkylamines

1-1-1 Introduction

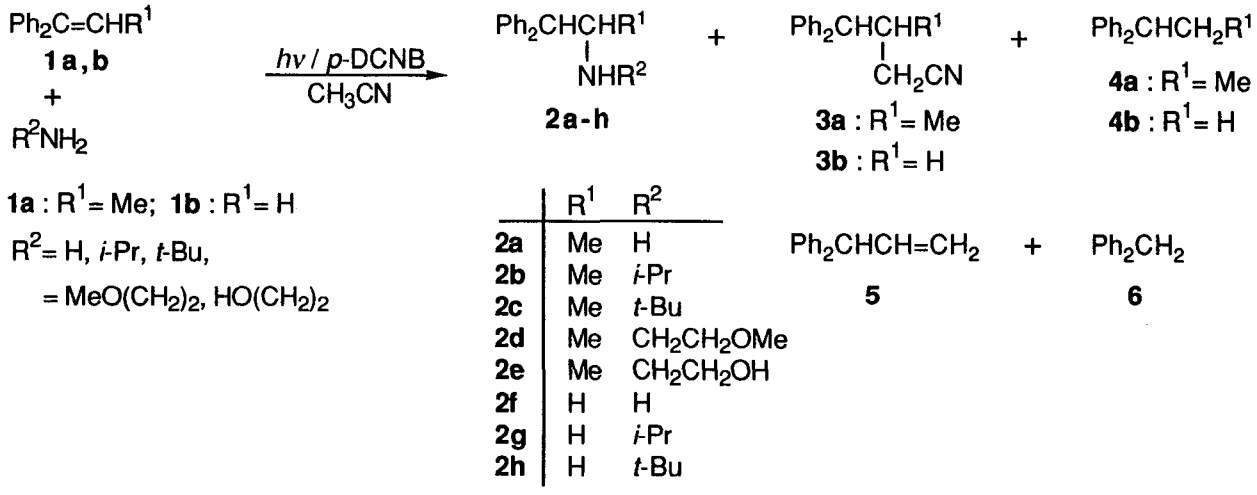
Photoinduced nucleophilic additions in the presence of electron acceptors have been investigated for variety of electron-donating substrates (D) involving aryl-substituted alkene, strained compounds, and arenes from mechanistic and synthetic points of view.[1] In general, a key pathway of photoinduced nucleophilic additions is the addition of nucleophiles (NuH) to the cation radicals of D ($D^{+\bullet}$) generated from a photoinduced electron transfer from D to electron acceptors (A), as shown in Scheme 1. While extensive studies on photoadditions using alcohols, water, and cyanide ion as nucleophiles have accumulated, little is known about the photoaddition of ammonia and amines, except for the author's reports on photoamination of arenes with ammonia and alkylamines which will be discussed in Chapter 2. Since amines serve as both a nucleophile and a base, their photoaddition is expected to show different features from other nucleophiles. In Chapter 1, the author reports on the photoaddition of ammonia and alkylamines to aryl-substituted alkenes (**1**) using *p*-dicyanobenzene (*p*-DCNB) as A.



Scheme 1.

1-1-2 Results and Discussion

The photoamination of diphenylalkene (**1**) was carried by irradiating a deaerated acetonitrile solution of **1**, *p*-DCNB, and ammonia or alkylamines through a Pyrex filter with a high-pressure mercury lamp; incident light was absorbed by both **1** and *p*-DCNB under these conditions. The results are summarized in Table 1 and Scheme 2. The photoamination of 1,1-diphenylpropene (**1a**) with ammonia, isopropylamine, 2-methoxyethylamine, and 2-aminoethanol gave the *N*-substituted 2-amino-1,1-diphenylpropanes (**2a-e**) accompanied by the formation of considerable amounts of 3-methyl-4,4-diphenylbutanenitrile (**3a**), 1,1-diphenylpropane (**4a**), 3,3-diphenylpropane (**5**), and diphenylmethane (**6**). Similarly, *N*-substituted 1-amino-2,2-diphenylethanes (**2f-h**), 4,4-diphenylbutanenitrile (**3b**), and 1,1-diphenylethane (**4b**) were formed from the photoamination of 1,1-diphenylethene (**1b**) with ammonia, isopropylamine, and *t*-butylamine. The photoamination of **1b** with 2-methoxyethylamine gave *N*-(2-methoxyethyl)-2,2-diphenylethylamine (**2i**) along with the formation of 1-(2-aminoethoxy)-3,3-diphenylpropane (**8**), **3b**, and **4b** (Scheme 3). In all cases, *p*-DCNB was mostly recovered after photoamination. It was confirmed that the photoamination which takes place to afford the aminated products (**2**) does not occur in the absence of an electron acceptor; e.g. the photoreaction of **1b** with isopropylamine in the absence of *p*-DCNB gave **3b**, **4b**, and 1,1-dimethyl-3,3-diphenylpropylamine (**9**) (Scheme 4).



	R^1	R^2
2a	Me	H
2b	Me	*i*-Pr
2c	Me	*t*-Bu
2d	Me	CH_2CH_2OMe
2e	Me	CH_2CH_2OH
2f	H	H
2g	H	*i*-Pr
2h	H	*t*-Bu

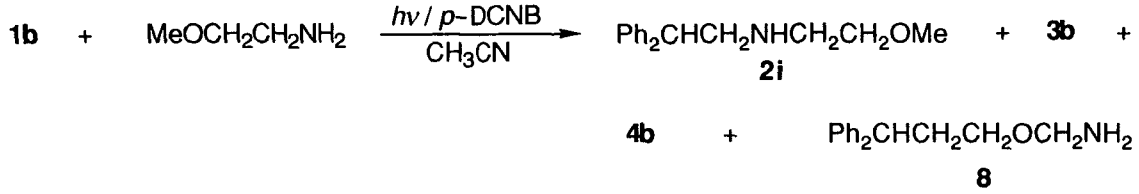
Scheme 2.

Table 1. Photoamination of Diphenylalkene (**1**) with Ammonia and Alkylamines in the Presence of *p*-Dicyanobenzene[a]

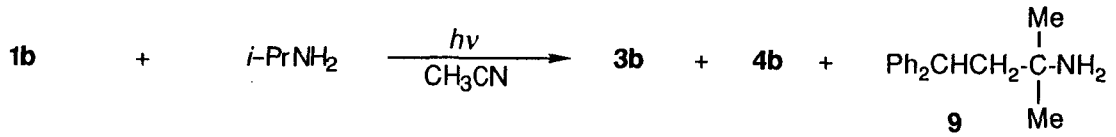
Run No.	**1**	RNH_2	Products (Yield[b] / %)								Conv. of **1**/%	Recov. of A/%
1	**1a**	NH_3	**2a** (44)	**3a** (7)			**5** (5)	**6** (23)			76	78
2	**1a**	*i*-$PrNH_2$	**2b** (65)	**3a** (3)	**4a** (2)		**5** (8)	**6** (6)			81	92
			2a (21)									
3	**1a**	*t*-$BuNH_2$		**3a** (72)							100	83
4[c]	**1a**	*t*-$BuNH_2$	**2c** (46)		**4a** (2)		**5** (9)	**6** (12)			59	90
5	**1a**	$MeO(CH_2)_2NH_2$	**2d** (55)	**3a** (tr)	**4a** (4)		**5** (10)	**6** (7)			74	89
6	**1a**	$HO(CH_2)_2NH_2$	**2e** (58)	**3a** (7)	**4a** (1)		**5** (3)	**6** (2)			69	87
7[d]	**1b**	NH_3	**2f** (18)	**3b** (15)	**4b** (tr)		**7** (41)				70	96
8	**1b**	*i*-$PrNH_2$	**2g** (48)	**3b** (27)	**4b** (12)						28	100
			2f (8)									
9	**1b**	*t*-$BuNH_2$	**2h** (22)	**3b** (60)							66	98
10	**1b**	$MeO(CH_2)_2NH_2$	**2i** (19)	**3b** (6)	**4b** (3)		**8** (20)				80	93
11[e]	**1b**	*i*-$PrNH_2$		**3b** (7)	**4b** (17)		**9** (32)				84	-
12[f]	**1b**	*i*-$PrNH_2$			**4b** (12)		**10** (48)	**11** (13)			76	3
							12a (28)	**12b** (7)				
13[g]	**1b**	*i*-$PrNH_2$	**2g** (68)	**3b** (21)	**4b** (9)						22	94
14[h]	**1b**	*i*-$PrNH_2$	**2g** (36)	**3b** (15)	**4b** (19)						39	86

[a] For deaerated acetonitrile solutions (150 mL) containing **1** (5.6 mmol), *p*-DCNB (16 mmol) and the amine (73 mmol). [b] Isolated yields based on consumed **1**. [c] For propanenitrile solution. [d] MeCN-H_2O (9:1) solution. [e] In the absence of *p*-DCNB. [f] For DMF solution. [g] Redox-photosensitization by phenanthrene; after the photoreaction, 13% of phenanthrene was recovered. *N*-Isopropyl-9-amino-9,10-dihydrophenanthrene (**13**) was isolated in 44% yield based on phenanthrene used. [h] Redox-photosensitization by triphenylene; 13% of triphenylene was recovered after the photoreaction.

Photoamination with isopropylamine gave both **2a** and **2b** from **1a**, and **2f** and **2g** from **1b** in addition to other products. Figure 1 shows plots of the yields of **2f**, **2g**, **3b**, and **4b** vs. the irradiation time for the photoamination of **1b** with isopropylamine; the yields of **3b** and **4b** increased with an increase in the conversion of **1b**, whereas the yield of **2f** gradually increased at the expense of **2g**.



Scheme 3.



Scheme 4.

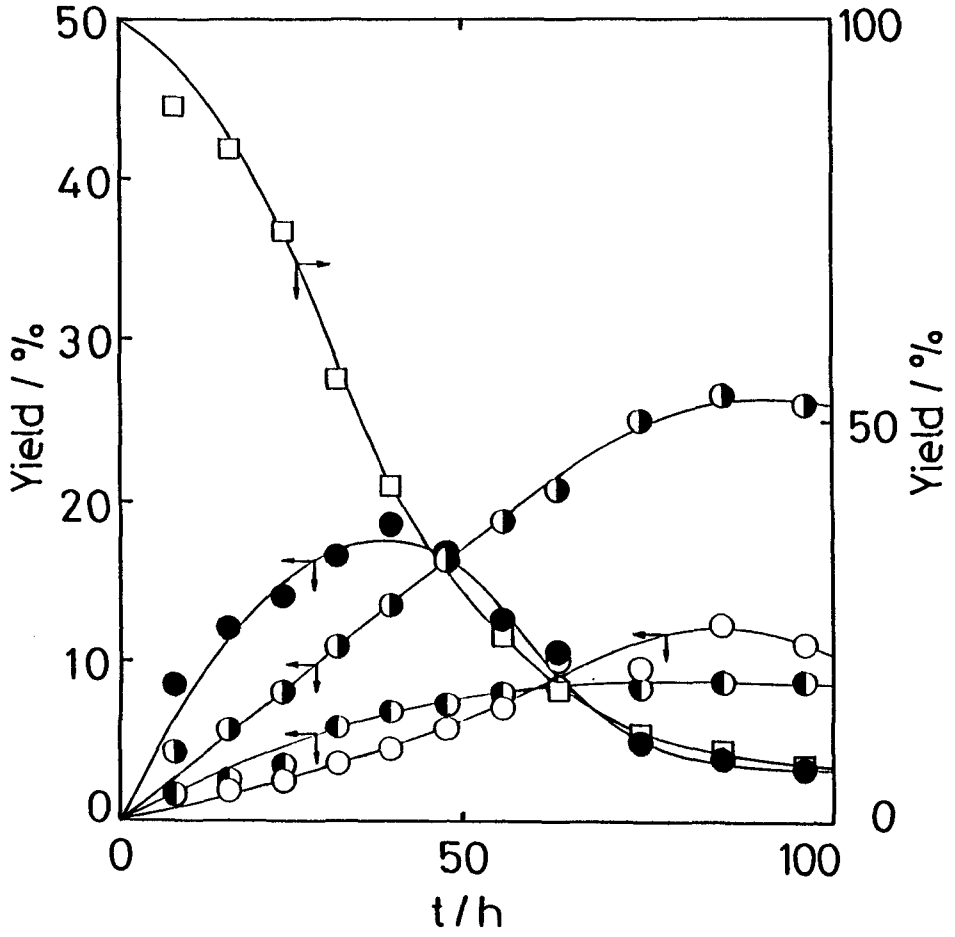
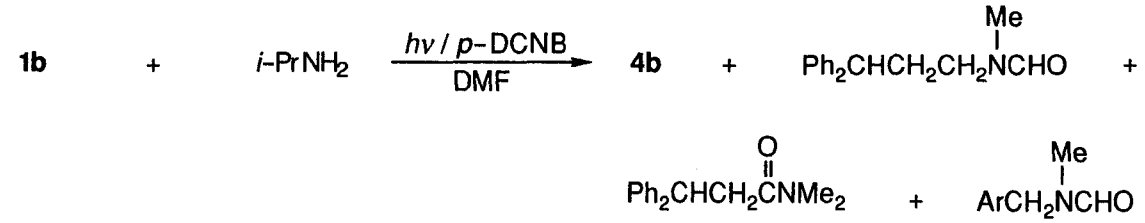


Fig. 1. Time-conversion plots for the disappearance of **1b** (-□-) and for the formation of **2f** (-○-), **2g** (-●-), **3b** (-◑-) and **4b** (-◐-) in the photoamination of **1b** with *i*-$PrNH_2$.

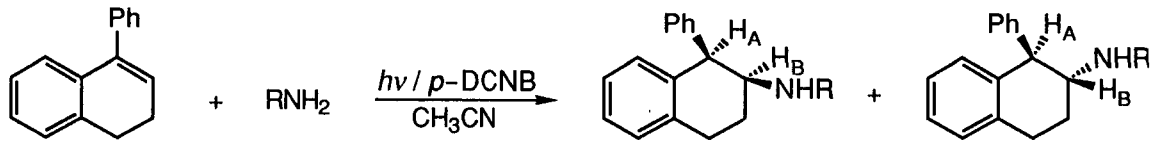
Although acetonitrile has been found to be an excellent solvent for the photoamination of arenes,[2] the photoamination of **1a** and **1b** in acetonitrile gave considerable amounts of acetonitrile-incorporated products (**3a,b**). It is noteworthy that the photoamination of **1a** and **1b** with *t*-butylamine gave **3a** and **3b** as the major products. It was also found that the photoamination of **1a** with *t*-butylamine occurred in propanenitrile to give **2c** without photoreaction with the nitrile group of the solvent. No photoamination of **1b** occurred in *N,N*-dimethylformamide (DMF), 1,2-dimethoxyethane, or benzene; the photoreaction of **1b** in DMF gave the adducts (**10**,**11**, and **12a,b**) of DMF with either **1b** or *p*-DCNB (Scheme 5).[2] In the photoamination of **1b** with ammonia in acetonitrile-water (9:1), 2,2-diphenylethanol (**7**) was produced in consequence to the photoaddition of water to **1b** along with the formation of **2f**.



Scheme 5.

Since electron-transfer photosensitization by 9,10-dicyanoanthracene (DCA),[3,4] 1-naphthonitrile (CNN)[5] or redox-photosensitization[6] by aromatic hydrocarbons have provided useful tools for the photoaddition of alcohols to a variety of aryl-substituted alkenes, these methods were attempted in the present photoamination. However, no photoamination of **1b** with isopropylamine occurred by DCA- or CNN-photosensitization. The redox-photosensitized reaction of **1b** with isopropylamine in the presence of *p*-DCNB using phenanthrene as a sensitizer gave **2g**, **3b**, and **4b** accompanied by the formation of *N*-isopropyl-9-amino-9,10-dihydrophenanthrene (**13**). When triphenylene was used as a sensitizer, the photoamination proceeded along with the consumption of triphenylene. Thus, the redox-photosensitized amination of **1b** using phenanthrene or triphenylene is inefficient because of the consumption of sensitizers.

In order to elucidate the stereochemistry of the addition of amines, the photoamination of 1-phenyl-3,4-dihydronaphthalene (**1c**) was performed. The photoamination of **1c** with ammonia, isopropylamine, and *t*-butylamine gave the corresponding *cis*- and *trans*-*N*-substituted 1-phenyl-2-amino-1,2,3,4-tetrahydronaphthalene (**14**,**15**, and **16**) (Scheme 6). The stereochemistries of **14**, **15**, and **16** were determined by their ^{1}H-NMR spectra. The signal for methine proton (H_A) on the C1 of trans isomers appeared at 0.35-0.50 ppm higher in field than that of cis-isomers. The upfield shift of H_A of trans isomers may be due to a shielding effect of lone-pair electrons on the adjacent nitrogen atom. Further support is that the vicinal coupling constants (J = 5.0-5.5 Hz) between H_A and H_B in cis isomers are smaller than those in trans isomers (J = 7.7-9.0 Hz). Though the ratio of the trans to the cis isomer was dependent on the bulkiness of amine, the cis isomers (**15a** and **16a**) were mainly produced in the cases of photoamination with isopropylamine and *t*-butylamine (Table 2).



14a ; R =H
15a ; R = *i*-Pr
16a ; R = *t*-Bu

14b ; R =H
15b ; R = *i*-Pr
16b ; R = *t*-Bu

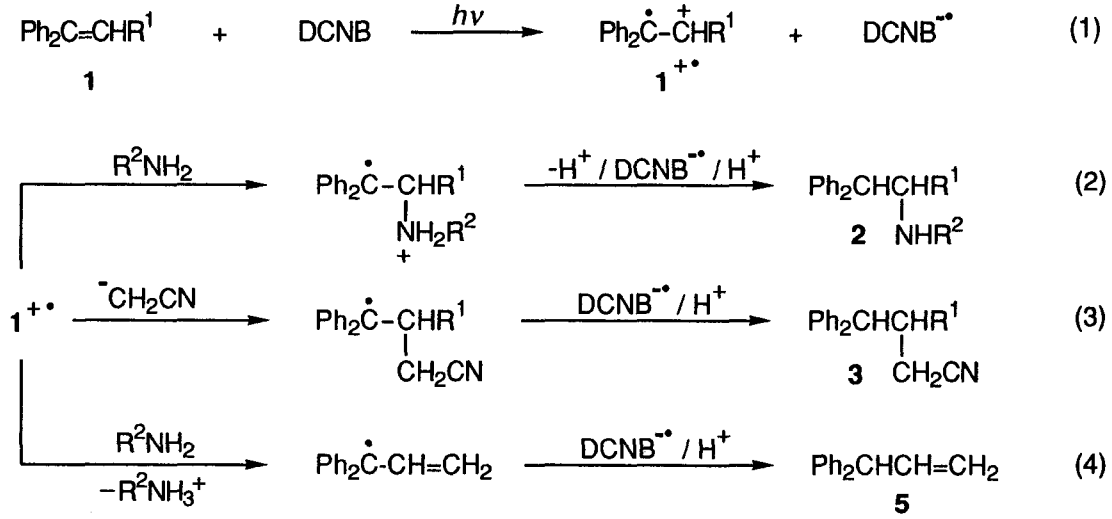
Scheme 6.

Table 2. Photoamination of 1-Phenyl-3,4-diphydronaphthalene (**1c**) with Ammonia and Alkylamines in the Presence of *p*-Dicyanobenzene

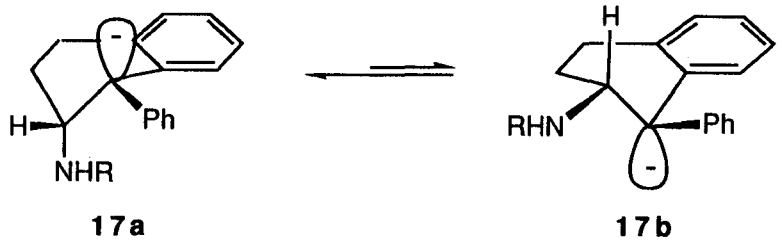
Run No.	RNH_2	Products (**a** : **b**)[b]	Yield[a] / %	Conv.of **1c** / %	Recov. of *p*-DCNB / %
15[c]	NH_3	**14** (49:51)	33	71	86
16	*i*-$PrNH_2$	**15** (75:25)	22	64	100
17	*t*-$BuNH_2$	**16** (79:21)	28	70	100

[a] Isolated yields based on consumed **1c**. [b] Isomer ratio of **a** to **b**. [c] MeCN-H_2O (9:1) solution.

The photoinduced electron transfer reaction from electron-rich substances to aromatic nitriles has been well known to occur in polar solvents.[1] It is proposed that such photoamination is initiated by a photoinduced electron transfer from **1** to *p*-DCNB, since no photoamination of **1** occurred in the absence of *p*-DCNB (Eq. 1). The cation radical of **1**, thus formed, react with RNH_2 to give aminated cation radicals which are reduced with the anion radical of *p*-DCNB and then protonated to afford **2** (Eq. 2).



In the case of **1c**, the resulting aminated anion (**17**) takes both **17a** and **17b** comformations, depending on the bulkiness of the amine, as shown in Scheme 7. The electron pair of **17** may exist in the axial position, which is favorable for a maximum orbital overlap of the electron pair with the aromatic ring. When an amino group has a bulky alkyl group, a steric



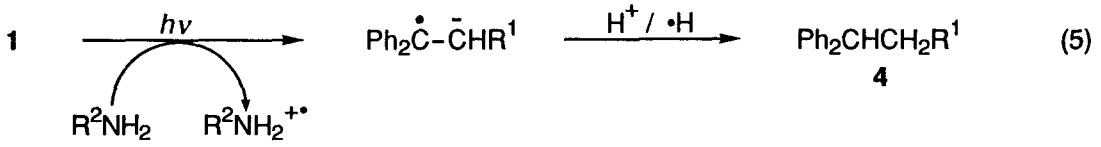
17a **17b**

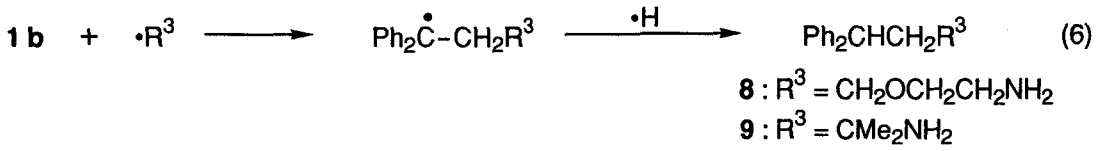
Scheme 7.

interation between the amino group on C-2 and the phenyl group on C-1 may be expected to favor **17a**, in which the amino group is axial and the phenyl group is equatorial. Therefore, the protonation of **17** affords mainly the cis isomer (**15a** and **16a**) in the photoamination of **1c** with isopropylamine or *t*-butylamine. This result is in accord with the results reported for the photoaddition of methanol to **1c**.[4)]

The fact that 4,4-diphenyl-2,2-dideuterio-1-butanenitrile was formed from the photoamination of **1b** in acetonitrile-d_3 reveals that the cyanomethyl group of **3** can undoubtedly be attributed to acetonitrile. Figure 1 shows that **3b** is the primary product from the photoreaction of **1b**. On the other hand, it has been reported that **3** was not formed at all from the photoaddition of water and alcohols to **1a** or **1b** in the presence of electron acceptors.[4,5)] Indeed, when *p*-DCNB was used as an electron acceptor, the photoaddition of **1b** in the absence of amines in acetonitrile gave only **7** in 41% yield without the formation of **3b**. These observations, therefore, suggest that $\mathbf{1}^{+\bullet}$ reacts with the cyanomethyl anion which is generated from the deprotonation of acetonitrile by the amine. The reduction of cyanomethylated radicals by the anion radical of *p*-DCNB gives **3** after protonation (Eqs. 3 and 7). Thus, $\mathbf{1}^{+\bullet}$ can undergo Eq. 3 competitively with Eq. 2, depending on the nature of RNH_2. *t*-Butylamine operates more effectively for the formation of **3** compared with other primary alkylamines since the bulky substituent may slow down the nucleophilic addition and/or the strong basicity may facilitate the protonation of acetonitrile. Also, amines oparate as a base for the isomerization of **1a** to **5**, which proceeds by deprotonation from $\mathbf{1a}^{+\bullet}$ with RNH_2 according to Eq. 4.

The photoreaction of **1b** with isopropylamine in the absence of *p*-DCNB would be initiated by a photoinduced electron transfer from isopropylamine to **1b** to give a cation radical of the amine and the anion radical of **1b**, as disucussed in previous reports.[7,8,9)] The protonation of the anion radical of **1b** and the subsequent hydrogen abstraction from such hydrogen sources as isopropylamine gave **4b** (Eq. 5). Equation 5 would take place to some extents, even for photoamination in the presnce of *p*-DCNB, since a considerable amount of **4b** was produced.





The formation of **9** would occur by the reaction of **1b** with 2-amino-2-propyl radical which is generated by deprotonation from the cation radical of isopropylamine or by a hydrogen abstraction from isopropylamine with radical species, as shown in Eq. 6. Similarly, the formation of **8** would occur by the reaction of **1b** with the 2-aminoethoxymethyl radical formed by hydrogen abstraction from 2-methoxyethylamine (Eq. 6). The formation of **3b** from the photoreaction in the presence of *p*-DCNB would occur by the reaction of **1b** with the cyanomethyl radical formed by hydrogen abstraction from acetonitrile by a radical species in reaction system; this mechanism is in accord with that for photochemical incorporation of acetonitrile to norbornene.[10)]

Degradation of secondary amines (**2b** and **2g**) to primary amines (**2a** and **2f**) can be attributed to the secondary reactions, as is shown in Fig. 1. It was confirmed that the photoreaction of isolated **2g** with *p*-DCNB gave **2f**. Degradation would occur through an electron transfer reaction from **2b** or **2g** to the excited singlet state of *p*-DCNB.[8)] Also, the formation of **6** occurred as a secondary reaction which proceeds by C-C bond cleavage of the cation radicals of **2a-e** generated by a photoinduced electron transfer to DCNB. This is in agreement with a mechanism which has been reported for the cleavage of tertiary amines[11)] and 2,2-diphenylethyl alkyl ethers.[12)]

Neither DCA- nor CNN-photosensitization was a useful method for the photoamination of **1**. From the fluorescence quenching of DCA or CNN with **1** or amines, it was found that the excited singlet state of DCA or CNN was efficiently quenched by ammonia and primary amines, as well as **1**. No occurrence of the DCA- or CNN-sensitized photoamination is attributed to the more efficient quenching of the excited singlet state of DCA or CNN by RNH_2 than that by **1** under the reaction conditions.

1-1-3 Experimental

^1H and ^{13}C NMR spectra were taken on a Bruker AC 250P for $CDCl_3$ solutions with tetramethylsilane used as an internal standard. The fluorescence and IR spectra were taken on a Hitachi MPF-4 and a JASCO A 302, respectively. A JEOL JMS-D300S was used for analyzing the mass spectra. GLC analysis was carried out on a Shimadzu GC-14A or a Hitachi 163 with flame-ionization detectors using a capillary column (CBP1-M25-025) or a 50 cm × 4 mm column of 2% silicone OV-17 on Chromosorb WAW DMCS.

Spectral grade acetonitrile was distilled from P_2O_5 and then from CaH_2. 1,1-Diphenylethene, *p*-dicyanobenzene, and amines were commercially available. 1,1-Diphenylpropene was prepared from the acid-fragmentation of 2,2-diphenyl-3-methyloxetane prepared from the photoaddition of benzophenone with 2-butene.[13] 1-Phenyl-3,4-dihydronaphthalene was prepared according to a method described in the literature.[14]

*Photoamination of **1a-b** with Amines.* Into a Pyrex vessel was introduced an acetonitrile solution (150 mL) containing **1** (5,6 mmol) and *p*-DCNB (16 mmol). The amine (73 mmol) was added to the solution after argon bubbling for 50 min, whereas an ammonia solution was obtained by dissolving gaseous ammonia into the solution. The solutions were irradiated for 8-50 h with an Eikosha PIH-300 high-pressure mercury lamp though Pyrex. After evaporation of the solvent, cool methanol was added to the residue and then unreacted *p*-DCNB was filtered off. The filtrate was chromatographed on silica gel with hexane to give **1**, **4**, **5**, and **6**. Further elution with hexane-benzene (4:1) gave **3**. The aminated products (**2a-i**) were obtained by elution with benzene-ethyl acetate (4:1) or acetone. Purification was carried out by either

recrystallization from hexane-benzene or vacuum distillation. The recrystallization of **2c** and **2h**, however, could not be achieved owing to failure regarding their acetylation. The structure of **2b**, **2d**, and **2e** were determined by comparison of the ^{1}H and ^{13}C NMR spectra with authentic samples prepared from the reaction of 1,1-diphenyl-3-propanone with the corresponding amines in the presence of sodium cyanoborohydride.[15] The structure of **4a**, **4b**, **5**,[16], **6**, **7**, and **13**[17] were determined by direct comparisons with authentic samples.

*1-Methyl-2,2-diphenylethylamine (**2a**)*: Mp 113.0-113.5 °C; ^{1}H NMR δ = 1.12 (3H, d, J = 6.4 Hz), 1.80 (3H, s), 3.84 (1H, d, J = 10.0 Hz), 4.83-4.93 (1H, m), 5.28 (1H, br d, J = 8.5 Hz), and 7.16-7.29 (10H, m); ^{13}C NMR δ = 20.4, 23.4, 47.4, 58.0, 126.72, 126.65, 128.1, 128.2, 128.6, 128.7, 141.8, 142.2, and 169.4; MS *m/z* 253 (M^+); IR ($CHCl_3$) 3430 and 1660 cm^{-1}; Found: C, 80.48; H, 7.29; N, 5.77 %. Calcd for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53 %.

*N-Isopropyl-(1-methyl-2,2-diphenylethyl)amine (**2b**)*: ^{1}H NMR δ = 0.98 (3H, d, J = 9.9 Hz), 1.00 (6H, d, J = 10.0 Hz), 2.71 (1H, br s), 2.82-2.92 (1H, m), 3.54-3.65 (1H, m), 3.80 (1H, d, J = 10.2 Hz), and 7.12-7.39 (10H, m); ^{13}C NMR δ = 18.7, 21.7, 24.2, 45.9, 53.2, 59.1, 126.4, 126.7, 128.3, 128.5, 128.8, 142.4, and 143.1; MS *m/z* 253 (M^+); mp 161.5-162.0 °C; IR ($CHCl_3$) 3430 and 1660 cm^{-1}; Found: C, 81.58; H, 8.46; N, 4.61 %. Calcd for $C_{20}H_{26}NO$: C, 81.31; H, 8.53; N, 4.74 %.

*N-t-Butyl-(1-methyl-2,2-diphenylethyl)amine (**2c**)*: ^{1}H NMR δ = 0.96 (9H, s,) 1.08 (3H, d, J = 5.8 Hz), 3.54-3.65 (1H, m), 3.70 (1H, d, J = 10.2 Hz), and 7.13-7.39 (10H, m); ^{13}C NMR δ = 22.5, 29.9, 51.1, 60.3, 126.3, 126.8, 128.5, 128.6, 142.6, and 143.0; MS *m/z* 267 (M^+).

*N-(2-Methoxyethyl)-(1-methyl-2,2-diphenylethyl)amine (**2d**)*: ^{1}H NMR δ = 1.00 (3H, d, J = 6.1 Hz), 2.61-2.70 (1H, m), 2.78-2.88 (1H, m), 3.17 (3H, s), 3.27-3.39 (2H, m), 3.40-3.51 (1H, m), 3.76 (1H, d, J = 10.2 Hz), and 7.09-7.38 (10H, m); ^{13}C NMR δ = 18.5, 46.6, 55.8, 58.4, 59.3, 71.7, 126.3, 126.6, 128.1, 128.2, 128.5, 128.7, 142.4, and 143.3; MS *m/z* 269 (M^+).

*N-(2-Hydroxyethyl)-(1-methyl-2,2-diphenylethyl)amine (**2e**)*: Mp 83.5-84.0 °C; ^{1}H NMR δ = 1.05 (3H, d, J = 6.1 Hz), 2.63-2.72 (1H, m), 2.74-2.89 (3H, m), 3.46-3.57 (3H, m), 3.78 (1H, d, J = 10.3 Hz), and 7.13-7.38 (10H, m); ^{13}C NMR δ = 18.5, 48.1, 55.9, 59.0, 60.6, 126.5, 126.8, 128.0, 128.1, 128.6, 128.9, 142.2 and 142.8; MS *m/z* 255 (M^+).

2,2-Diphenylethylamine (**2f**): Mp 89.5-90.0 °C; ^{1}H NMR δ = 1.82 (3H, s), 3.84 (1H, d, J = 7.9 Hz), 3.86 (1H, d, J = 7.9 Hz), 4.17 (1H, d, J = 7.9 Hz), 5.67 (1H, br s), and 7.16-7.33 (10H, m); ^{13}C NMR δ = 23.2, 43.9, 50.5, 126.8, 128.0, 128.7, 141.9, and 170.2; MS *m/z* 239 (M^+); The acetamide of **2f** was unambiguously identified by a direct comparison with an authentic sample.

*N-Isopropyl-2,2-diphenylethylamine (**2g**)*: The acetamide; Mp 104.5-105.0 °C; ^{1}H NMR δ = 0.78 and 1.18 (6H, d, J = 6.8 and 6.9 Hz), 1.58 and 2.21 (3H, s), 3.78 and 3.87 (2H, d, J = 7.5 and 7.0 Hz), 3.74-3.82 and 4.11-4.20 (1H, m), 4.14 and 4.69 (1H, t, J = 7.0 and 7.5 Hz), and 7.13-7.39 (10H, m); ^{13}C NMR δ = 20.3 and 20.9, 22.3 and 22.6, 47.3 and 49.1, 48.4 and 51.6, 49.6 and 52.5, 126.3 and 126.9, 128.2 and 128.7, 128.6 and 132.7, 142.3 and 143.1, and 171.2; MS *m/z* 281 (M^+); IR ($CHCl_3$) 1620 cm^{-1}; Found: C, 80.79; H, 8.51; N, 5.07 %. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98 %.

*N-t-Butyl-2,2-diphenylethylamine (**2h**)*: ^{1}H NMR δ = 1.14 (9H, s), 3.28 (2H, d, J = 8.0 Hz), 4.30 (1H, t, J = 8.0 Hz), 4.70 (1H, br s), and 7.19-7.35 (10H, m); ^{13}C NMR δ = 27.4, 46.9, 50.5, 52.1, 126.8, 128.0, 128.7, and 142 0; MS *m/z* 253 (M^+).

*N-(2-Methoxyethyl)-2,2-diphenylethylamine (**2i**)*: A colorless oil, ^{1}H NMR δ = 2.81 (2H, t, J = 5.3 Hz), 3.25 (2H, d, J = 7.7 Hz), 3.30 (3H, s), 3.42 (2H, t, J = 5.3 Hz), 4.21 (1H, t, J = 7.7 Hz), and 7.14-7.38 (10H, m); ^{13}C NMR δ = 49.1, 54.5, 58.6, 71.7, 126.5, 127.9, 127.9, 128.6, and 142.8; MS *m/z* 255 (M^+); the acetamide: Found: C, 76.98; H, 7.58; N, 4.98 %. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71 %.

*3-Methyl-4,4-diphenylbutanenitrile (**3a**)*: Mp 55.0-55.5 °C; ^{1}H NMR δ = 1.07 (3H, d, J = 6.5 Hz), 2.10 (1H, dd, J = 16.7 and 7.0 Hz), 2.33 (1H, dd, J = 16.7 and 3.8 Hz), 2.62-2.79 (1H, m), 3.65 (1H, d, J = 11.4 Hz), and 7.12-7.31 (10H, m); ^{13}C NMR δ = 18.3,

23.5, 34.2, 57.6, 118.5, 126.6, 126.9, 127.6, 127.8, 128.7, 129.0, 142.5, and 142.6; MS *m/z* 235 (M^+); IR ($CHCl_3$) 2220 cm^{-1}

*4,4-Diphenylbutanenitrile (**3b**)*: ^1H NMR δ = 2.20 (2H, t, J = 7.5 Hz), 2.30-2.45 (2H, m), 4.03 (1H, t, J = 7.9 Hz), and 7.10-7.31 (10H, m); ^{13}C NMR δ = 15.7, 31.0, 49.8, 119.3, 126.8, 127.7, 128.8, and 142.8; MS *m/z* 221 (M^+); IR ($CHCl_3$) 2190 cm^{-1}. The structure of **3b** was determined by a comparison with an authentic sample prepared from the cyanation of 3,3-diphenyl-1-propanol according to a reported method.[18)]

*1-(2-Aminoethoxy)-3,3-diphenylpropane (**8**)*: The acetamide: Mp 64.5-65.0 °C (from hexane-benzene); ^1H NMR δ = 1.95 (3H, s), 2.28-2.36 (2H, m), 3.34-3.39 (6H, m), 4.09 (1H, t, J = 7.9 Hz), 5.89 (1H, br s) and 7.15-7.37 (10H, m); ^{13}C NMR δ = 23.2, 35.2, 39.3, 47.5, 69.1, 69.3, 126.3, 127.8, 128.5, 144.4, and 170.1; MS *m/z* 297 (M^+); IR ($CHCl_3$) 3440 and 1660 cm^{-1}; Found: C, 76.73; H, 7.63; N, 4.66%. Calcd for $C_{19}H_{23}NO_2$: C, 76.73; H, 7.80; N, 4.71 %.

*1,1-Dimethyl-3,3-diphenylpropylamine (**9**)*: The acetamide: Mp 120.5-121.0 °C (from hexane-benzene); ^1H NMR δ = 1.29 (6H, s), 1.44 (3H, s), 2.53 (2H, d, J = 7.1 Hz), 4.05 (1H, t, J = 7.0 Hz), 5.38 (1H, br s), and 7.18-7.29 (10H, m); ^{13}C NMR δ = 23.4, 27.3, 44.1, 47.2, 53,2, 125.6, 126.7, 128.1, 145.0, and 169.1; MS *m/z* 255 (M^+); IR ($CHCl_3$) 3440 and 1660 cm^{-1}; Found: C, 81.26; H, 8.46; N, 4.82%. Calcd for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98 %.

*Photoreaction of **1b** in N,N-Dimethylformamide.* After irradiation, the photolysates were dissolved in 150 mL of benzene; then, *N,N*-dimethylformamide was extracted with six 50 mL portions of water. After evaporation of benzene, the residue was chromatographed on silica gel with hexane to give **1b** and **4b**. Further elution with benzene gave **10** and **11**. **12a** and **12b** were obtained by elution with benzene-ethyl acetate (8:1). **11** and **12b** could not be purified from the mixture of either **10** and **11** or **12a** and **12b**.

*N-(3,3-Diphenylpropyl)-N-methylformamide (**10**)*: The acetamide: Mp 60.0-61.0 °C (from hexane-benzene); ^1H NMR δ = 2.30 and 2.33 (2H, m), 2.85 and 2.86 (3H, s), 3.17 and 3.28 (2H, t, J = 6.9 and 7.7 Hz), 3.86 and 3.94 (1H, t, J = 7.9 and 7.8 Hz), 7.14-7.33

(10H, m), and 7.60 and 7.98 (1H, s); ^{13}C NMR δ = 29.4 and 32.5, 33.5 and 34.7, 43.5 and 47.6, 48.0 and 49.1, 126.4 and 126.7, 127.6 and 127.7, 128.6 and 128.8, 143.5 and 144.1, 162.4 and 162.8; MS *m/z* 253 (M^+); IR ($CHCl_3$) 1665 cm^{-1}; Found: C, 80.65; H, 7.53; N, 5.79 %. Calcd for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53 %.

*N,N-Dimethyl-3,3-diphenylpropanamide (**11**)*: ^1H NMR δ = 2.86 (6H, s), 3.04 (2H, d, J = 7.5 Hz), 4.68 (1H, t, J = 7.4 Hz), and 7.13-7.32 (10H, m); ^{13}C NMR δ = 35.5, 37.2, 39.3, 47.2, 126.3, 127.8, 128.8, 144.3, 171.2; MS *m/z* 253 (M^+); IR ($CHCl_3$) 1645 cm^{-1}.

*N-(4-Cyanobenzyl)-N-methylformamide (**12**)*: A colorless oil, ^1H NMR δ = 2.80 and 2.91 (3H, s), 4.49 and 4.58 (2H, s), 7.35-7.38 (2H, d, J = 8.0 Hz), and 7.64-7.69 (2H, d, J = 8.0 Hz), 8.20 and 8.26 (1H, s); ^{13}C NMR δ = 29.7 and 34.3, 47.6 and 53.0, 111.6 and 112.2, 118.3 and 118.6, 128.0 and 128.7, 132.5 and 132.8, 141.5 and 141.7, 162.78 and 162.82; MS *m/z* 174 (M^+); IR ($CHCl_3$) 2230 and 1660 cm^{-1}; Found: C, 68.84; H, 5.89; N, 16.26 %. Calcd for $C_{10}H_{10}N_2O$: C, 68.94; H, 5.79; N, 16.08 %.

*N-(3-Cyanobenzyl)-N-methylformamide (**12b**)*: ^1H NMR δ = 2.83 and 2.96 (3H, s), 4.64 and 4.77 (2H, s), 7.27-7.50 (2H, m), 7.57-7.74 (2H, m), 8.20 and 8.34 (1H, s); ^{13}C NMR δ = 29.6 and 34.5, 45.8 and 51.4, 112.1 and 112.3, 116.9 and 117.4, 128.3 and 128.8, 128.9 and 132.6, 132.8 and 133.4 139.5 and 139.9, 162.9 and 163.0; MS *m/z* 174 (M^+); IR ($CHCl_3$) 2230 and 1660 cm^{-1}.

*Photoamintion of **1c***. In a similar manner to the case of **1a**, the photoamination of **1c** was performed for an acetonitlile solution (50 mL) containing **1c** (2.5 mmol), *p*-DCNB (2.5 mmol), and the amine (25 mmol). After irradiation, aminated products were obtained by extraction with dilute hydrochloric acid. The acidic aqueous layer was basified with saturated $NaHCO_3$ followed by extraction with diethyl ether. Evaporation of the ether left crude aminated products. **1c** and *p*-DCNB were recovered from benzene solutions and were chromatographed on silica gel with hexane and benzene. A mixture of **14a** and **14b** was acetylated with Ac_2O, and recystallized from hexane-benzene to give the acetamide of **14a**. Also, **15a** was obtained in the same way, though the acetamide of **16** was not purified by recystallization.

*cis-2-Amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (**14a**)*: ^{1}H NMR δ = 1.62 (2H, br s), 2.03-2.15 (2H, m), 2.88-3.12 (2H, m), 3.32 (1H, ddd, J = 8.1, 5.4, and 5.2 Hz), 4.22 (1H, d, J = 5.2 Hz), and 6.68-7.40 (9H, m); ^{13}C NMR δ = 28.3, 31.0, 51.7, 56.1, 125.9, 126.3, 126.5, 127.9, 128.5, 130.6, 130.8, 136.3, 138.3, and 141.7.

*trans-2-Amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (**14b**)*: ^{1}H NMR δ = 1.62 (2H, br s), 1.72-1.85 (2H, m), 2.88-3.12 (2H, m), 3.20 (1H, ddd, J = 10.4, 9.0, and 3.0 Hz), 3.73 (1H, d, J = 9.0 Hz), and 6.68-7.40 (9H, m); ^{13}C NMR δ = 28.0, 28.5, 50.5, 54.5, 125.9, 126.0, 126.7, 128.6, 128.7, 129.6, 130.2, 136.3, 138.8, and 144.4. The acetamide: Mp 196.5-198.0 °C; Found: C, 81.41; H, 7.32; N, 5.16%. Calcd for $C_{18}H_{19}NO$: C, 81.48; H, 7.22; N, 5.28 %.

*cis-N-Isopropyl-2-amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (**15a**)*: ^{1}H NMR δ = 1.00 (3H, d, J = 6.0 Hz), 1.03 (3H, d, J = 6.0 Hz), 1.26 (1H, br s), 1.57-1.83 (2H, m), 3.00-3.05 (2H, m), 3.12 (1H, q, J = 6.0 Hz), 3.21 (1H, ddd, J = 11.7, 5.0, and 3.3 Hz) 4.36 (1H, d, J = 5.0 Hz), and 6.92-7.37 (8H, m); ^{13}C NMR δ = 23.0, 23.1, 25.0, 28.9, 44.4, 48.5, 53.3, 125.8, 126.3, 127.8, 128.6, 130.5, 130.8, 136.6, 139.0, and 141.9.

*trans-N-Isopropyl-2-amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (**15b**)*: ^{1}H NMR δ = 0.82 (3H, d, J = 6.2 Hz), 1.01 (3H, d, J = 6.2 Hz), 1.26 (1H, br s), 2.05-2.14 (2H, m), 2.80-2.92 (2H, m), 3.00-3.05 (1H, m), 3.06-3.09 (1H, m), 3.91 (1H, d, J = 7.7 Hz), 6.74 (1H, d, J = 7.7 Hz), and 6.92-7.37 (8H, m); ^{13}C NMR δ = 22.4, 24.2, 26.9, 27.3, 45.6, 52.6, 57.4, 125.9, 126.0,m 126.5, 128.4, 128.5, 129.4, 130.7, 136.6, 138.4, and 144.7; The acetamide: Mp 143.5-145.0 °C; Found: C, 88.24; H, 7.93; N, 4.61%. Calcd for $C_{21}H_{25}NO$: C, 82.04; H, 8.20; N, 4.56 %.

*cis-N-t-Butyl-2-amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (**16a**)*: ^{1}H NMR δ = 1.09 (9H, s), 1.40 (1H, br s), 1.61-1.91 (2H, m), 2.99-3.05 (2H, m), 3.20 (1H, ddd, J = 11.6, 5.5, and 3.5 Hz), 4.12 (1H, d, J = 5.5 Hz), 6.91 (1H, d, J = 7.7 Hz), and 7.03-7.36 (8H, m); ^{13}C NMR δ = 28.6, 29.1, 30.0, 50.8, 51.0, 51.5, 125.7, 126.2, 126.2, 127.6, 128.6, 130.8, 131.0, 136.5, 139.5, and 142.5.

*trans-N-t-Butyl-2-amino-1-phenyl-1,2,3,4-tetrahydronaphthalene (**16b**)*: ^{1}H NMR δ = 0.87 (9H, s), 1.40 (1H, br s), 2.13-2.24 (2H, m), 2.93 (2H, t, J = 5.0 Hz), 2.99-3.05 (1H, m), 3.77 (1H, d, J = 9.0 Hz), 6.73 (1H, d, J = 7.5 Hz), and 7.03-7.36 (8H, m); ^{13}C NMR δ = 28.3, 29.8, 30.0, 51.0, 54.2, 55.4, 125.7, 126.0, 126.6, 127.7, 128.4, 129.8, 130.9, 137.0, 139.2, and 144.7.

1-2 Photoamination of Stilbene Derivatives with Ammonia

1-2-1 Introdution

Nucleophilic addition induced by photoinduced electron transfer has received much attention as a potentially useful procedure for organic synthesis.[1] Especially regio- and stereoselective photoinduced nucleophilic additions have high synthetic potential. The regiochemistry for anti-Markovnikov addition of nucleophiles to aryl substituted alkenes (e.g., 1,1-diphenylethylene) [4, 5a, c, 19] and aryl-substituted cyclopropane[20] has been attributed to the conjugative stabilization by aryl groups for the adduct radicals (or cation radicals) formed from the reaction of nucleophile with the cation radicals. However, there are few studies on the regiochemistry of the photoinduced nucleophilic addition to the delocalized cation radicals such as arenes and stilbene derivatives,[21] since the addition of typical nucleophiles such as alcohols to the cation radicals is very inefficient.[22]

Recently, Yasuda et al applied the photoamination of stilbene to the synthesis of isoquinoline compounds such as benzylisoquinolines or isopavines.[23] Thus, ammonia and amines are such strong nucleophiles that they can add to the delocalized cation radicals. Therefore, the author has investigated here on the regiochemistry of the photoinduced nucleophilic addition to a dozen 1,2-diarylethenes using ammonia as nucleophile.

1-2-2 Results and Discussion

The photoamination of 1,2-diarylethenes (**18a-l**) with ammonia was carried out by irradiating a degassed acetonitrile-water or acetonitrile-benzene-water solution containing **18a-l**, *p*-DCNB, and ammonia through a Pyrex filter by a high-pressure mercury lamp at room temprature (Scheme 8). An incident light was almost absorbed by **18** under these conditions. Upon the irradiation the isomerization from *trans*-**18** to *cis*-**18** immediately occurred up to the photostaionary state where cis isomers are rich. Therefore, a mixture of trans amd cis isomer of **1** was used for photoaminations. After the photoamination, *p*-DCNB was mostly recoverd.

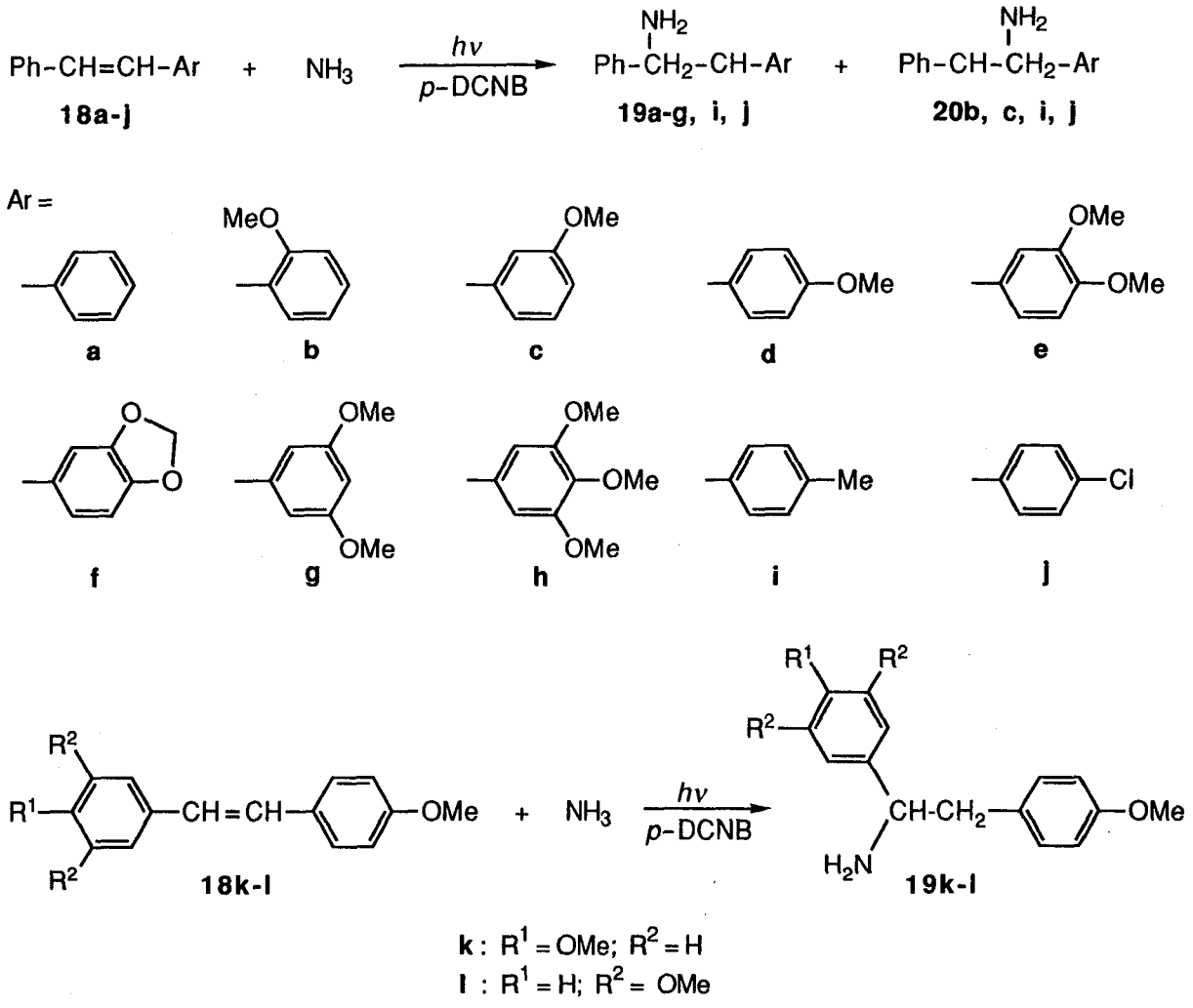
No photoamination in the absence of *p*-DCNB occurred at all. The results of photoamination are summarized in Table 3. The photoaminations proceeded in relatively good yields except for photoaminations of **18e**, **18f**, and **18l**. But no photoamination of **18h** occurred. It should be noted that the photoamination proceeds in MeCN-benzene-H_2O (8:1:1 and 7:2:1) more efficiently than in MeCN-H_2O (9:1).

The photoamination of stilbene (**18a**) and *p*,*p*'-dimethoxystilbene (**18k**) gave 1-amino-1,2-diphenylethane (**19a**) and 1-amino-1,2-bis(*p*-methoxyphenyl)ethane (**19k**), respectively.

Table 3. Photoamination of Stilbene Derivatives (**18**) with Ammonia in the Presence of *p*-Dicyanobenzene[a]

18 ($E_{1/2}^{ox}$ / V)[b]	Solvent[c]	Irradn. time / %	Yield[d] / % (**19** : **20**)	Recov.of **18** / %, (*Z*:*E*)	Recov. of *p*-DCNB/ %
18a (1.10)	9:0:1	20	46	14 (9:1)	97
18a	7:2:1	31	88	3 (1:1)	96
18b (0.91)	9:0:1	7	59 (1:0.4)	0	97
18c (1.06)	9:0:1	10	80 (1:0.7)	1 (1:1)	99
18c	8:1:1	20	91 (1:0.7)	2 (1:1)	91
18d (0.79)	9:0:1	21	53 (1:0)	6 (2:1)	97
18d	8:1:1	15	62 (1:0)	12 (4:1)	89
18e (0.68)	9:0:1	20	21 (1:0)	69 (4:1)	88
18f (0.75)	8:1:1	20	21 (1:0)	21 (2:1)	100
18g (1.09)	9:0:1	20	28 (1:0.7)	7 (5:1)	75
18g	7:2:1	17	60 (1:0.7)	2 (2:1)	82
18h (0.72)	9:0:1	20	0	70 (5:1)	88
18i (0.99)	7:2:1	20	87 (1:0.6)	0	92
18j (1.13)	7:2:1	8	54 (1:0.9)	6 (1:2)	100
18k (0.64)	7:2:1	41	44	5 (2:1)	100
18l (0.79)	7:2:1	20	16 (1:0)	59 (1:0)	85

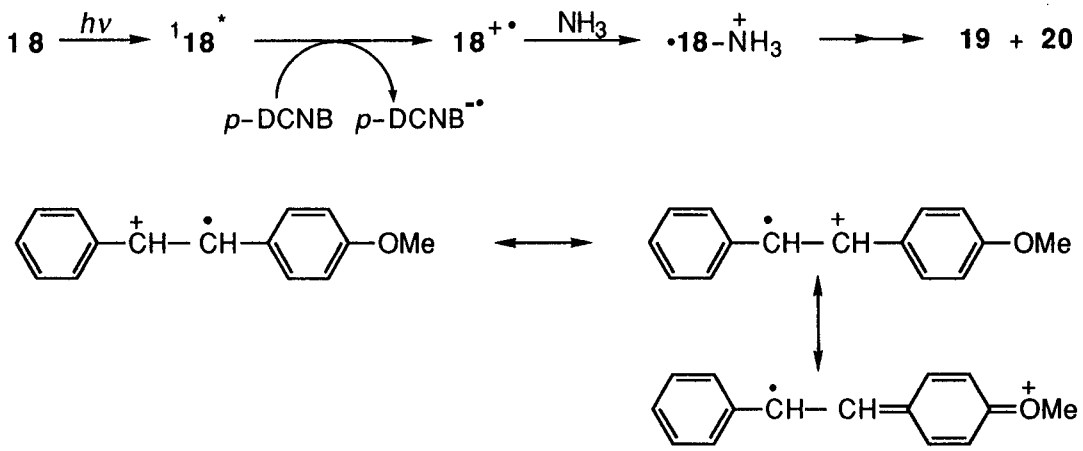
[a] A MeCN-benzene-H_2O solution (70 mL) containing **18** (7 mmol) and *p*-DCNB (7 mmol) was bubbled with ammonia and then irradiated. [b] Half-peaks of oxidation potentials vs $Ag/AgNO_3$ for the trans isomer of **18**. [c] The values are the ratio of MeCN-benzene-H_2O. [d] Isolated yields based on **18** used.



Scheme 8.

The photoaminations of 1-aryl-2-phenylethenes **18b**, **18c**, and **18g** having the methoxy group at the ortho or meta position gave both 1-amino-2-aryl-1-phenylethane **19** and 1-amino-1-aryl-2-phenylethane **20** in a ratio of 1 : 0.4-0.9. On the other hand, the photoamination of *p*-methoxystilbene (**18d**) gave 1-amino-2-(*p*-methoxyphenyl)-1-phenylethene (**19d**) selectively in contrast with the case of *p*-methyl or *p*-chlorostilbenes (**18i,j**) which gave both **19** and **20**. Similarly, the photoamination of **18e-f** having an alkoxy group at the para position gave the corresponding 1-amino-2-aryl-1-phenylethanes (**19e-f**) selectively. Also, the photoamination of 1-(*p*-methoxyphenyl)-2-(3,5-dimethoxyphenyl)ethene (**18l**) with ammonia gave selectively 1-amino-1-(3,5-dimethoxyphenyl)-2-(*p*-methoxyphenyl)ethane (**19l**).

Stern-Volmer quenching studies show that *p*-DCNB quenches the excited singlet state of **18** (**18***) at a nearly diffusion-controlled rate, and the free energy changes for the electron transfer from ^{1}**18*** to *p*-DCNB are calulated to be negative by the Rehm-Weller equation[24] using the oxidation potentials ($E_{1/2}^{ox}$) of Table 3. Therefore, the photoamination is certainly initiated by photoinduced electron transfer from ^{1}**18*** to *p*-DCNB to give the cation radical of **18** (**18**$^{+\bullet}$) and the anion radical of *p*-DCNB (*p*-DCNB$^{-\bullet}$). The nucleophilic addition of ammonia to **18**$^{+\bullet}$ gives the aminated cation radicals, which are deprotonated and undergo reduction by DCNB$^{-\bullet}$ followed by protonation to afford the final aminated products **19** and/or **20**.



Scheme 9.

The positive charge of **18**$^{+\bullet}$ might develop over two benzylic positions and aromatic rings, depending on the substituent on aryl group. In the cation radicals of **18d** having methoxy group at the para position, the positive charge might populate at benzylic position of the phenyl group to a greater extent than at benzylic position of the *p*-methoxyphenyl group, since the photoamination occurred selectively at the benzylic position of phenyl group. The positive charge on the benzylic position of the *p*-methoxyphenyl group decreases by the resonance with the methoxy group at the para position which results in the localization of positive charge on the oxygen of methoxy groups (Scheme 9). Similary, the positive charge on the cation radicals of **18e-f** might populate at the benzylic position of the phenyl group to a

greater extent than at the benzylic position of the aryl proups to result in the selective photoamination. The inefficient photoaminations of **18e, 18f,** and **18h** arise from the the fact that the positive charge of the cation radicals distributes over the aryl groups more predominantly than over the olefinic moiety. In the case of the other stilbene derivatives **18b, 18c, 18g, 18i,** and **18j** the positive charge might deverop over both the bezylic positions of aryl and phenyl groups, resulting in formation of both **19** and **20.** Thus, it is found that the methoxy group on the para position affects strongly the regioselectivity for the photoamination of stilbene derivatives.

1-2-3 Experimental

Fluorescence spectra were taken on a Hitachi MPF-4. Fluorescence lifetimes were measured on a Horiba NAES 550 by a single-photon counting method. Oxidation potentials were measured in acetonitrile on a Hokuto Denko HA-501G and HB-105 as potentiostat and function generator using a three-electrode cyclic voltammetric cell; the working electrode, platinum disk; the counter electrode, carbon electrode; the reference electrode, $Ag/AgNO_3$.

The preparation of stilbene derivatives (**18b-l**) was performed by Wittig reaction of substituted benzaldehydes with phosphonium salts according to the literature method[25] expect for the commercially available *trans*-**18a**.

trans-18b: Mp 56.0-57.0 °C (from hexane-benzene) (Lit.[25] mp 58.6-59.5 °C); ^{13}C NMR δ = 55.52, 110.96, 120.75. 123.52, 126.42, 126.47, 126.56, 127.34, 128.58, 128.65, 129.11, 137.98, and 156.94.

trans-18c: Mp 37.0-38.0 °C (from hexane-benzene); ^{13}C NMR δ = 55.24, 111.74, 113.29, 119.24, 126.54, 127.68, 128.57, 128.68, 129.00, 129.63, 137.21, 138.78, and 159.88; Found: C, 85.68; H, 6.71 %. Calcd for $C_{15}H_{14}O$: C, 85.57; H, 6.60 %.

trans-18d: Mp 135.0-137.0 °C (from hexane-benzene) (Lit.[25] mp 136.2-137.0 °C); ^{13}C NMR δ = 55.32, 114.17, 126.26, 126.67, 127.21, 127.72, 128.23, 128.64, 130.21, 137.70, and 159.36.

trans-18e: Mp 129.0-130.0 °C (from methanol); ^{13}C NMR δ = 55.85, 55.93, 108.72, 111.20, 119.89, 126.27, 126.81, 127.29, 128.45, 128.66, 130.44, 137.51, 148.91, and 149.91; Found: C, 79.95; H, 6.69 %. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71 %.

trans-18f: Mp 96.2-96.5 °C (from benzene); ^{13}C NMR δ = 101.12, 105.56, 108.42, 121.47, 126.31, 127.02, 127.36, 129.35, 129.66, 131.89, 137.41, 147.31, and 148.15; Found: C, 80.20; H, 5.35 %. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.25 %.

trans-18g: Mp 59.0-60.0 °C (from methanol); ^{13}C NMR δ = 55.37, 100.02, 104.62, 126.58, 127.73, 128.68, 129.22, 137.15, 139.37, and 161.00; Found: C, 79.84; H, 6.67 %. Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.67 %.

trans-18h: Mp 109.0-110.0 °C (from benzene); ^{13}C NMR δ = 56.18, 60.97, 103.76, 126.45, 127.60, 128.24, 128.71, 133.13, 137.27, 138.15, and 153.47; Found: C, 75.48; H, 6.69 %. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71 %.

trans-18i: Mp 122.0-122.5 °C (from hexane-benzene) (Lit.[26] mp 119.2-119.8 °C); ^{13}C NMR δ = 21.45, 126.39, 126.41, 127.39, 127.67, 128.63, 129.39, 134.53, and 137.49.

trans-18j: Mp 132.5-133.0 °C (from hexane-benzene) (Lit.[26] mp 129.2-129.6 °C); ^{13}C NMR δ = 126.54, 127.34, 127.65, 127.86, 128.73, 128.83, 129.29, 123.16, 135.83, and 136.96.

trans-18k: Mp 218.0-220.0 °C (from methanol) (Lit.[26] mp 212.0-213.5 °C); ^{13}C NMR δ = 55.32, 114.12, 126.20, 127.42, 130.51, and 159.03.

trans-18l: Mp 56.5-57.5 °C (from methanol); ^{13}C NMR δ = 55.34, 99.61, 104.33, 114.14, 126.56, 127.80, 128.74, 129.92, 139.70, 159.39, and 160.96; Found: C, 75.40; H, 6.70 %. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71 %.

*Photoamination of **18a-l**. Genaral Procedure.* In 140 mL of acetonitrile-water (9:1) or acetonitrile-benzene-water (7:2:1 or 8:1:1) was dissolved a mixture of **18** (7 mmol) and *p*-DCNB (7 mmol), and then ammonia gas was bubbled into the solutions. The solutions were irradiated with an Eikosha PIH-300 high-pressure mercury lamp through Pyrex under cooling with water. Details of the followup process was described in Chapter 2. We could not separate

the acetoamides of **19** and **20** by column chromatography on silica gel or recrystallization. Therefore, the assignments of **19** and **20** were performed by the ^{13}C NMR spectra.

*Acetamide of **19a***: Mp 143.0-144.0 °C (from hexane-benzene); ^{1}H NMR δ = 1.91 (3H, s), 3.09 (2H, d, J = 7.2 Hz), 5.26 (1H, q, J = 7.2 Hz), 6.06 (1H, br s), 7.03-7.06 (2H, m), and 7.18-7.36 (8H, m); ^{13}C NMR δ = 23.25, 42.52, 54.55, 126.56, 126.66, 127.40, 128.33, 128.55, 129.30, 137.34, 141.50, and 169.37; MS *m/z* 239 (M^+), 196 (M-Ac), 148 (M-$PhCH_2$).

*Acetamide of **19b***: Mp 136.0-137.0 °C (from hexane-benzene); ^{13}C NMR δ = 23.34, 41.65, 54.44, 55.16, 113.71, 126.66, 127.31, 127.82, 128.50, 129.28, 130.26, 141.63, 158.23, and 169.28; Found: C, 76.02; H, 7.13; N, 5.21 %. Calcd for $C_{17}H_{19}O_2N$: C, 75.81; H, 7.11; N, 5.20 %.

*Acetamide of **20b***: ^{13}C NMR δ = 23.34, 42.46, 53.94, 55.24, 113.88, 126.50, 128.50, 129.30, 129.31, 133.70, 137.52, 158.77, and 169.20.

*Acetamide of **19c***: ^{13}C NMR δ = 23.39, 42.53, 54.26, 55.08, 112.27, 114.75, 121.66, 127.41, 128.55, 129.29, 138.76, 141.46, 159.49, and 169.26.

*Acetamide of **20c***: ^{13}C NMR δ = 24.02, 42.47, 54.36, 55.20, 112.60, 112.67, 118.84, 126.53, 128.33, 129.60, 137.26, 143.15, 159.69, and 169.26.

*Acetamide of **19d***: Mp 145.0-146.0 °C (from methanol); ^{1}H NMR δ = 1.96 (3H, s), 3.06 (2H, d, J = 7.1 Hz), 3.77 (3H, s), 5.23 (1H, dt, J = 7.3 and 7.6 Hz), 6.06 (1H, br d), 6.77 (2H, d, J = 8.6 Hz), 6.97 (2H, d, J = 8.6 Hz), and 7.20-7.35 (m, 5H); ^{13}C NMR δ = 23.26, 41.63, 54.72, 55.20, 113.78, 126.69, 127.56, 128.56, 129.24, 130.29, 141.51, 158.33, and 169.45; MS *m/z* 269 (M^+), 226 (M-Ac), 211 (M-NHAc); Found: C, 75.55; H, 7.07; N, 5.18 %. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20 %.

*Acetamide of **19e***: Mp 140.0-141.0 °C (from methanol); ^{1}H NMR δ = 1.97 (3H, s), 3.03 (1H, dd, J = 13.6 and 7.1 Hz), 3.09 (1H, dd, J = 13.6 and 6.4 Hz), 3.70 (3H, s), 3.83 (3H, s), 5.24 (1H, q, J = 7.1 Hz), 5.89 (1H, br d), 6.42 (1H, s), 6.59 (1H, d, J = 8.1 Hz), 6.75 (1H, d, J = 8.1 Hz), and 7.17-7.30 (3H, m); ^{13}C NMR δ = 23.38, 42.11, 54.52, 55.72, 55.86, 111.07, 112.62, 121.42, 126.75, 127.42, 128.58, 129.58, 141.39, 147.81, 148.71,

and 169.34; MS *m/z* 299 (M^+), 241 (M-NHAc); Found: C, 71.98; H, 7.02; N, 4.63 %. Calcd for $C_{18}H_{21}NO_3$: C, 72.21; H, 7.07; N, 4.68 %.

Acetamide of ***19f***: ^{1}H NMR δ = 1.96 (3H, s), 3.02 (2H, d, J = 7.08 Hz), 5.20 (1H, q, J = 7.6 Hz), 5.88 (1H, br d), 5.90 (2H, s), 6.00 (1H, d, J = 7.7 Hz), 6.53 (1H, s), 6.67 (1H, d, J = 7.7 Hz), and 7.16-7.37 (5H, m); ^{13}C NMR δ = 23.42, 42.21, 54.64, 100.85, 108.07, 109.61, 122.31, 126.64, 127.46, 128.60, 130.99, 141.35, 146.21, 147.54, and 169.29; MS *m/z* 282 (M-1), 223.

Acetamide of ***19g***: ^{13}C NMR δ = 23.04, 42.82, 54.47, 55.12, 98.73, 107.33, 126.73, 127.19, 128.41, 140.00, 142.00, 160.60, and 169.71.

Acetamide of ***20g***: ^{13}C NMR δ = 2.98, 42.60, 54.81, 55.18, 99.02, 104.97, 126.41, 128.23, 129.24, 137.78, 144.54, 160.82, and 169.71.

Acetamide of ***19i***: ^{13}C NMR δ = 21.03, 23.37, 42.06, 54.38, 126.63, 127.34, 128.52, 129.04, 129.16, 134.05, 136.07, 141.58, and 169.35.

Acetamide of ***20i***: ^{13}C NMR δ = 21.07, 23.37, 42.41, 51.18, 126.50, 126.57, 128.30, 129.24, 129.31, 137.06, 137.42, 138.40, and 169.29.

Acetamide of ***19j***: ^{13}C NMR δ = 23.38, 41.76, 54.53, 126.69, 127.65, 128.68, 130.63, 132.38, 135.80, 140.90, and 169.38.

Acetamide of ***20j***: ^{13}C NMR δ = 23.31, 42.38, 53.85, 126.78, 128.01, 128.43, 128.48, 129.24, 133.09, 136.79, 140.09, and 169.38.

Acetamide of ***19k***: Mp 154.0-155.0 °C; ^{1}H NMR δ = 1.93 (3H, s), 2.99 (1H, dd, J = 13.7 and 7.3 Hz), 3.06 (1H, dd, J = 13.7 and 6.9 Hz), 3.77 (3H, s), 3.79 (3H, s), 5.17 (1H, q, J = 7.3 Hz), 5.99-6.02 (1H, br d, J = 7.8 Hz), 6.75-6.85 (4H, m), 6.96 (2H, d, J = 8.6 Hz), and 7.13 (2H, d, J = 6.4 Hz); ^{13}C NMR δ = 23.32, 41.59, 54.14, 55.17, 55.25, 113.71, 133.90, 127.85, 129.48, 130.29, 133.70, 158.22, 158.79, and 169.25; MS *m/z* 296, 241.

Acetamide of ***19l***: ^{1}H NMR δ = 1.92 (3H, s), 2.99 (2H, d, J = 7.0 Hz), 3.73 (6H, s), 3.76 (3H, s), 5.15 (1H, t, J = 7.0 Hz), 5.87 (1H, br d), 6.26 (1H, s), 6.34 (2H, s), 6.76 (2H, d, J = 8.6 Hz), and 6.79 (2H, d, J = 8.6 Hz); ^{13}C NMR δ = 23.35, 41.54, 54.62,

55.32, 98.99, 104.89, 113.76, 130.27, 160.04, 129.24, 144.12, and 169.36; and 143.1; MS *m/z* 329 (M^+), 270 (M-NH_2Ac).

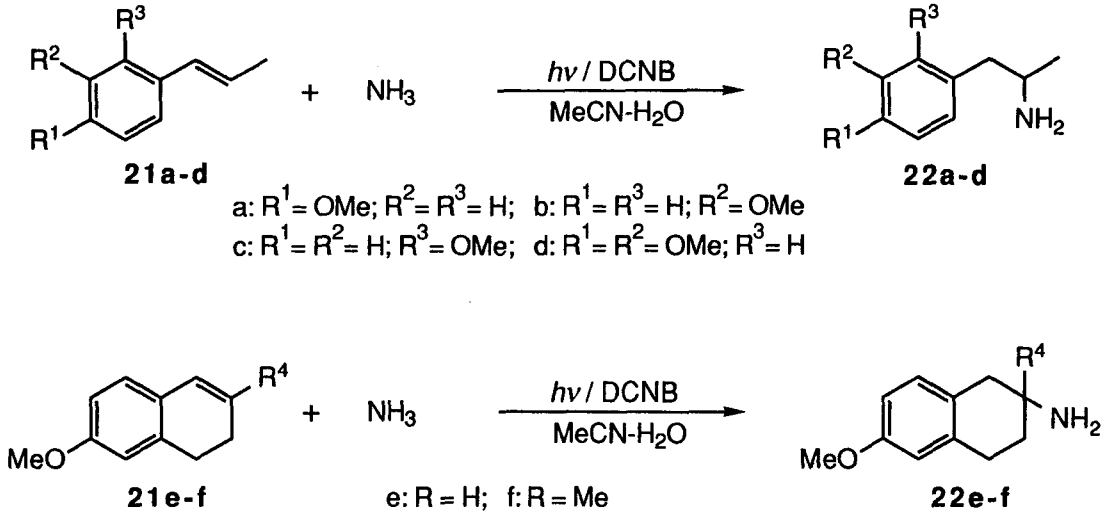
1-3 Photoamination of Styrene Derivatives with Ammonia

1-3-1 Introduction

Photoinduced nucleophilic additions have provided a useful synthetic tool to introduce a certain functional group to various electron-rich substrates.[27] We have been interested in the preparation of various aminated compounds by the photoamination of electron rich substrates. Construction of phenethylamine moiety has been extensively studied owing to their biological activity.[28] The photoamination of styrene derivatives may provide a useful synthetic tool for the preparation of phenethylamine derivatives. However, the nucleophilic addition of styrene derivatives by a photoinduced electron transfer, in general, proceeds in poor yields.[5] In this Section, the author reports the effective method for photoamination of styrene derivatives (**21**) with ammonia by a photoinduced electron transfer.

1-3-2 Results and Discussion

The photoaminations of **21** were performed by irradiating an ammonia-saturated acetonitrile-water solution containing **21** and *p*-DCNB or *m*-dicyanobenzene (*m*-DCNB) by a high-pressure mercury lamp through a Pyrex filter under cooling with water. The results are summarized in Table 4. The photoamination of *trans*-anethole (**21a**) with ammonia gave exclusively 1-(*p*-methoxyphenyl)-2-propylamine (**22a**) in 52% yield. Similarly the photoaminations of *trans*-1-arylpropenes (**21b-d**) and 7-methoxyl-1,2-dihydronaphthalenes (**21e, f**) gave selectively the corresponding 1-aryl-2-propylamines (**22b-d**) and 2-amino-6-methoxy-1,2,3,4-tetrahydronaphthalenes (**22e, f**), respectively (Scheme 10). The yields of **22** were improved by the addition of 1,3,5-triphenylbenzene (TPB; $E_{1/2}^{ox}$ = 1.52V) or *m*-terphenyl (*m*-TP; $E_{1/2}^{ox}$ = 1.52V), but other arenes such as 1,2,4-triphenylbenzene (1,2,4-TPB; $E_{1/2}^{ox}$ = 1.54V), *p*-terphenyl (*p*-TP; $E_{1/2}^{ox}$ = 1.51V) and biphenyl (BP; $E_{1/2}^{ox}$ = 1.54V) were not as effective as TPB or *m*-TP, as shown in Table 4. The amination of TPB itself did not occur at all to result in recovery of most of TPB after the photoreaction. The photoreaction



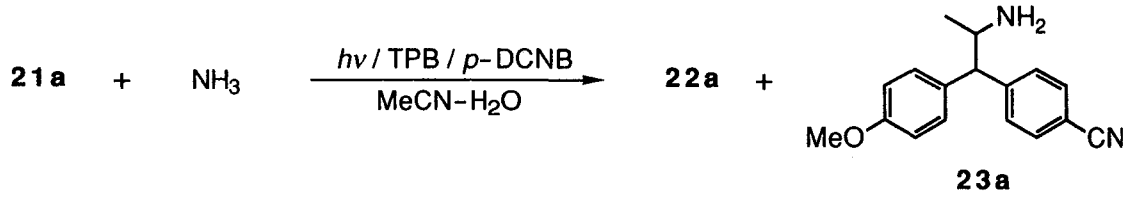
Scheme 10.

Table 4. Photoamination of Styrene Derivatives (**21a-f**)[a]

21	($E_{1/2}^{ox}$ / V)[b]	Additive[c]	DCNB	Product Yield[d] / %			Conv.of **21** / %
21a	(0.93)	TPB	*m*-DCNB	**22a**	91	(52)	98
21a		*m*-TP	*m*-DCNB	**22a**	85		98
21a		1,2,4-TPB	*m*-DCNB	**22a**	67		87
21a		*p*-TP	*m*-DCNB	**22a**	66		97
21a		BP	*m*-DCNB	**22a**	58		100
21b	(1.18)	TPB	*p*-DCNB	**22b**	46	(28)	93
21c	(0.86)	TPB	*p*-DCNB	**22c**	75	(68)	92
21d	(0.82)	TPB	*m*-DCNB	**22d**	65	(26)	100
21e	(0.81)	TPB	*m*-DCNB	**22e**	29	(23)	100
21f	(0.69)	TPB	*m*-DCNB	**22f**	48	(42)	89

[a] Irradiation of an ammonia-saturated acetonitrile-water (9:1; 75 mL) solution containing **21** (2 mmol), DCNB (3.75 mmol), and additive (0.75 mmol) for 4-24h. The additive arenes and DCNB were recovered in more than 60%. [b] The oxidation potentials vs $Ag/AgNO_3$ in acetonitrile. [c] Additive arenes. See text. [d] Isolated yields based on consumed **21**. The values in parenthesis are the yields for the photoamination in the presence of DCNB without TPB.

in the absence of DCNB did not give **22** at all. Under these reaction conditions incident light was almost absorbed by **21** even in the presence of TPB or *m*-TP; while 1,2,4-TPB, *p*-TP or BP absorbed incident light appreciably. In the cases of **21a,d-f**, *m*-DCNB was used as an electron acceptor, because the photoamination in the presence of *p*-DCNB resulted in substantial consumption of *p*-DCNB and the formation of *p*-cyanophenyl group-incorporated compound. The photoamination of **21a**, for example, gave 1-(*p*-methoxyphenyl)-1-(*p*-cyanophenyl)-2-propylamine (**23a**) in 29% yield along with the formation of **22a** (18%) (Scheme 11).

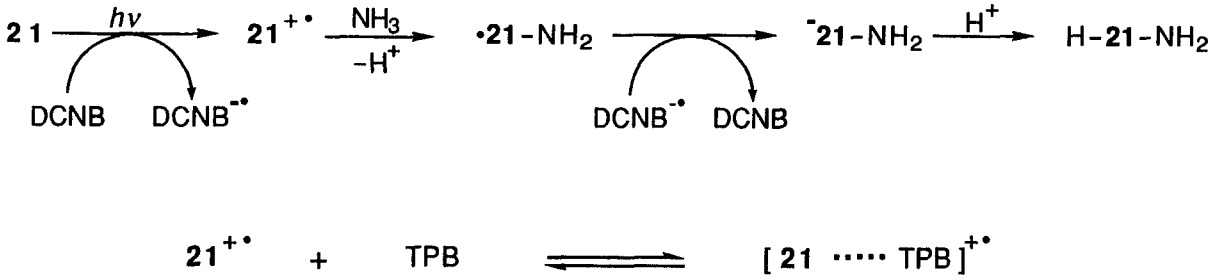


Scheme 11.

As has been reported for the photoamination of 1,1-diphenylalkenes and stilbenes in previous section, the photoaminations of **21** were initiated by a photoinduced electron transfer from **21** to DCNB to give a cation radical of **21** ($\mathbf{21}^{+\bullet}$) and an anion radical of DCNB ($DCNB^{-\bullet}$), because the oxidation potentials of **21** were relatively low and no photoamination occurred in the absence of DCNB. Thus the resulting $\mathbf{21}^{+\bullet}$ undergoes the nucleophilic addition of ammonia to form the aminated cation radical ($\bullet\mathbf{21}\text{-}NH_2$) which is reduced by $DCNB^{-\bullet}$ and followed by protonation to give **22** (Scheme 12). The incorporation of *p*-cyanophenyl group can be easily interpreted in terms of a radical coupling reaction between *p*-$DCNB^{-\bullet}$ and $\bullet\mathbf{21}\text{-}NH_2$ to form **23a**, as reported for other photoinduced nucleophilic additions.[20, 21, 29]

In the presence of TPB or *m*-TP, the improvement of the yields was achieved by the stabilization of $\mathbf{21}^{+\bullet}$ due to π-complex formation with the arenes to suppress side reactions such as dimerization. Similar effect due to π-complex formation was observed in the photoamination of stilbenes in which the yields of the aminated products were improved by use of benzene as co-solvent in Section 1-2. BP has been used as a cosensitizer for 9,10-

dicyanoanthracene (DCA)-photosensitized oxygenation: the cation radicals of BP ($BP^{+\bullet}$) generated by a photoinduced electron transfer from BP to DCA produce efficiently the cation radicals of substrates by a hole transfer from $BP^{+\bullet}$ to substrates.[30] However, the present additive effect of TPB or *m*-TP is different from that of the cosensitizer, because the yields of the aminated products were not improved by the addition of BP, 1,2,4-TPB, or *p*-TP, though the cation radicals of these arenes may be formed by a photoinduced electron transfer from these arenes to DCNB. Probably a hole transfer from these cation radicals to **21** occurs inefficiently because of reduction of these cation radicals by ammonia.



Scheme 12.

The efficient photoinduced nucleophilic addition of styrene derivatives can be successfully achieved by the addition of arenes in some cases. Therefore, the present amination will be a useful tool for the preparation of phenethylamine and aminotetralin derivatives.[31]

1-3-3 Experimental

A general procedure for isolation of **22** is as follows: After evaporation of acetonitrile, the residue was treated with acetic anhydride and pyridine to protect the amino group of **22**. The acetylated product, unreacted **21**, DCNB, and additive arenes were isolated by chromatography on silica gel. The spectral data of **22a-e** and **23a** are described as follows:

The acetamide of ***22a***: ^{1}H NMR (250 MHz, $CDCl_3$) δ = 1.09 (3H, d, J= 6.7 Hz), 1.93 (3H, s), 2.63 (1H, dd, J= 13.6, and 7.2 Hz), 2.77 (1H, dd, J= 13.6, and 5.7 Hz), 3.78 (3H, s), 4.20 (1H, m), 5.74 (1H, br d, J= 7.7 Hz), 6.83 (1H, d, J= 8.5 Hz), and 7.08 (2H, d, J=

8.5 Hz); ^{13}C NMR (62.9MHz, $CDCl_3$) δ = 19.81, 23.29, 41.44, 46.40, 55.2, 113.85, 129.98, 130.38, 158.28, and 170.01; Found: *m/z* 207.1258. Calcd for $C_{12}H_{17}NO_2$: M, 207.1255.

The acetamide of ***22b***: ^1H NMR (250MHz, $CDCl_3$) δ = 1.07 (3H, d, *J*= 6.7 Hz), 1.89 (3H, s), 2.62 (1H, dd, *J*= 13.4 and 7.3 Hz), 2.98 (1H, dd, *J*= 13.4 and 7.6 Hz), 3.75 (3H, s), 4.20 (1H, m), 5.68 (1H, br s), 6.71 (3H, m), and 7.17 (1H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 19.95, 23.42, 42.42, 46.11, 55.16, 111.77, 115.12, 121.82, 129.34, 139.59, 159.60, and 169.56; Found: *m/z* 207.1258. Calcd for $C_{12}H_{17}NO_2$: M, 207.1255.

The acetamide of ***22c***: ^1H NMR (250 MHz, $CDCl_3$) δ = 1.15 (3H, d, *J*= 6.6 Hz), 1.86 (3H, s), 2.72 (1H, dd, *J*= 13.5 and 5.9 Hz), 2.81 (1H, dd, *J*= 13.5 and 7.6 Hz), 3.84 (3H, s), 4.12-4.23 (1H, m), 5.95 (1H, br s), 6.85-6.98 (2H, m), and 7.10-7.24 (2H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 20.64, 23.47, 36.44, 46.62, 55.32, 110.45, 120.72, 126.76, 127.83, 131.18, 157.42, and 169.43; Found: *m/z* 207.1259. Calcd for $C_{12}H_{17}NO_2$: M, 207.1255.

The acetamide of ***22d***: ^1H NMR (250 MHz, $CDCl_3$) δ = 1.11 (3H, d, *J*= 6.6 Hz), 1.94 (3H, s), 2.63 (1H, dd, *J*= 13.6 and 7.3 Hz), 2.80 (1H, dd, *J*= 13.6 and 5.6 Hz), 3.86 (6H, s), 4.16-4.27 (1H, m), 5.52 (1H, br d), and 6.75 (3H, m); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 19.94, 23.48, 42.01, 46.21, 55.88, 111.14, 112.53, 121.42, 132.27, 147.65, 248.83, and 169.44; Found: *m/z* 237.1364. Calcd for $C_{13}H_{19}NO_3$: M, 237.1365.

22e: A colorless oil; ^1H NMR (250 MHz, $CDCl_3$) δ = 1.25-1.89 (3H, m), 2.45-2.46 (1H, d, *J*= 2.5 Hz), 2.68-2.76 (1H, m), 2.83-2.98 (1H, m), 3.13-3.16 (1H, d, *J*= 7.5 Hz), 3.76 (3H, s), and 6.91-6.95 (1H, d, *J*= 10.0 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 26.8, 28.1, 35.3, 43.8, 55.2, 111.9, 113.8, 128.6, 132.9, 139.5, and 157.6; The acetamide: Found: *m/z* 219.1172. Calcd for $C_{13}H_{17}NO_2$: M, 219.1258.

The acetamide of ***22f***: A colorless oil; ^1H NMR (250 MHz, $CDCl_3$) δ = 1.26 (1H, s), 1.49 (3H, s) 1.63-1.77 (1H, m), 1.87 (3H, s), 2.50-2.60 (1H, m), 2.75 (1H, d, *J*= 7.6 Hz), 2.81 (2H, s), 3.77 (3H, s), 5.35 (1H, s), 6.65-6.72 (2H, m), and 6.96 (1H, d, *J*= 8.3 Hz); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 24.36, 25.38, 26.35, 31.69, 41.82, 52.50, 55.21,

112.28, 113.33, 125.61, 130.43, 136.85, 157.93, and 170.18; Found: *m/z* 233.1413. Calcd for $C_{14}H_{19}NO_2$: M, 233.1414.

The diastereomeric mixture of the acetamide of ***23a***: ^{13}C NMR (62.9 MHz, $CDCl_3$) δ = 20.09 and 20.44, 23.17 and 23.26, 47.12 and 47.43, 55.24, 57.08 and 57.60, 110.19 and 110.45, 114.24 and 114.39, 118.75 and 118.87, 128.78 and 128.92, 129.13 and 129.20, 132.27 and 132.39, 132.52 and 132.94, 148.16 and 148.33, 158.64 and 158.70, 169.83 and 169.94; Found: *m/z* 308.1524. Calcd for $C_{19}H_{20}N_2O$: M, 308.1520.

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Chapter 2

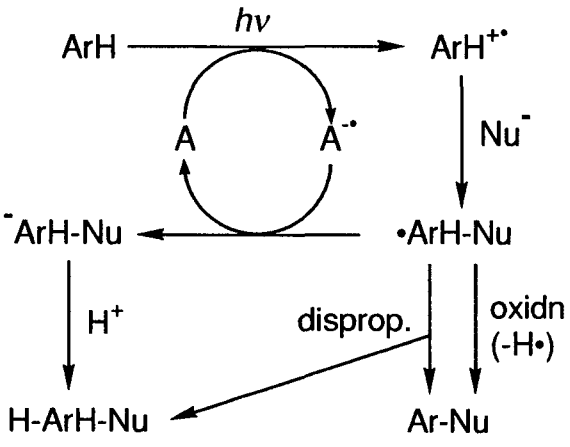
Photoinduced Nucleophilic Addition to Arenes via Electron Transfer

2-1 Photoamination of Arenes with Ammonia and Primary Amines

2-1-1 Introduction

Photoinduced electron transfer has received much attention as a convenient method for genaration of ion radicas, thus having potential application to oraganic synthesis.[1] To apply photoinduced electron transfer synthetically, the possibility of adding nucleophiles to photogenerated cation radical has been extensively explored.[2] If nucleophilies efficiently add to aromatic cation radicals, useful synthetic tools can be developed to achieve the direct introduction of functional groups to aromatic nuclei (Scheme 1). Indeed, Yasuda et al reported that a variety of arenes (ArH) are efficiently cyanated with NaCN[2a] and reduced by $NaBH_4$[2b] upon irradiation in the presence of *p*-dicyanobenzene.

In Chapter 2, the author wish to report the nucleophilic addition of ammonia and primary amines to the photogenerated cation radical of arenes. This photoamination is of synthetic significance, since direct amination of arenes is limited to Friede-Crafts reactions with activated amination reagents or to nucleophilic addition of amide anion to highly activated arenes.[3] The preparation of aromatic amines is usually carried out by reduction of



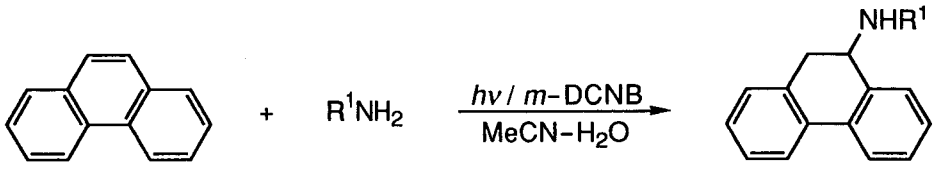
Scheme 1.

nitro, azo, and azide arenes or by substitution of halogen, hydroxy, and alkoxy groups in thermal or photochemical reactions.[3,4] Recently it was reported that substituted benzenes can be directly aminated by hydroxylamine-*O*-sulfonic acid and ferrous sulfate in acidic media.[5] From the synthetic point of view, a more general method is needed for direct amination of aromatic nuclei using ammonia and unactivated amines as amination reagents. The photoamination of arenes following Scheme 1 (Nu= NH_2 and NHR) seems to meet this requirement. Therefore, the author has thoroughly investigated the direct photoamination of various arenes with ammonia and aliphatic amines to establish its synthetic scope and limitations.

$$\underset{\mathbf{1}}{\mathrm{ArH}} + \mathrm{RNH_2} \xrightarrow[\mathrm{MeCN\text{-}H_2O}]{h\nu\,/\,m\text{-DCNB}} \underset{\mathbf{2}\text{ or }\mathbf{3}}{\mathrm{H\text{-}ArH\text{-}NHR}} + \underset{\mathbf{4}}{\mathrm{Ar\text{-}NHR}}$$

2-1-2 Results and Discussion

*Photoamination of Phenanthrene (**1a**) with Ammomia and Primary Amines.* In attempts to find optimum reaction condition, control experiments were performed for the photoamination of phenanthrene (**1a**) with ammonia in the presence of electron acceptors. Either acetonitrile or *N*,*N*-dimethylformamide was found to be a better solvent since the photoamination was efficient and clean, while methanol is a poor solvent. Moreover, photoamination yields were improved in the presence of water, as shown in Table 1. Therefore, we used 9:1 acetonitrile-water as solvent throughout the present investigation. As the electron acceptor, *m*-dicyanobenzene (*m*-DCNB) was genarally used because of the occurrence of relatively clean reactions compared with results from other electron acceptors tested, whereas 1-cyanonaphthalene (CNN) and 9,10-dicyanoanthracene (DCA) were found to be effective in the photoamination of *m*-dimethoxybenzene (**1l**) and biphenyl (**1m**), respectively.



1a **2a-m**

	R^1		R^1		R^1
2a	H	**2e**	*t*-Bu	**2i**	CH_2CH_2CN
2b	Me	**2f**	CH_2Ph	**2j**	CH_2CH_2OH
2c	Et	**2g**	CH_2CH_2Ph	**2k**	$CH_2CH_2NH_2$
2d	*i*-Pr	**2h**	$CH_2CH{=}CH_2$	**2l**	CH_2CH_2NHAc
				2m	CH_2CO_2Et

Scheme 2.

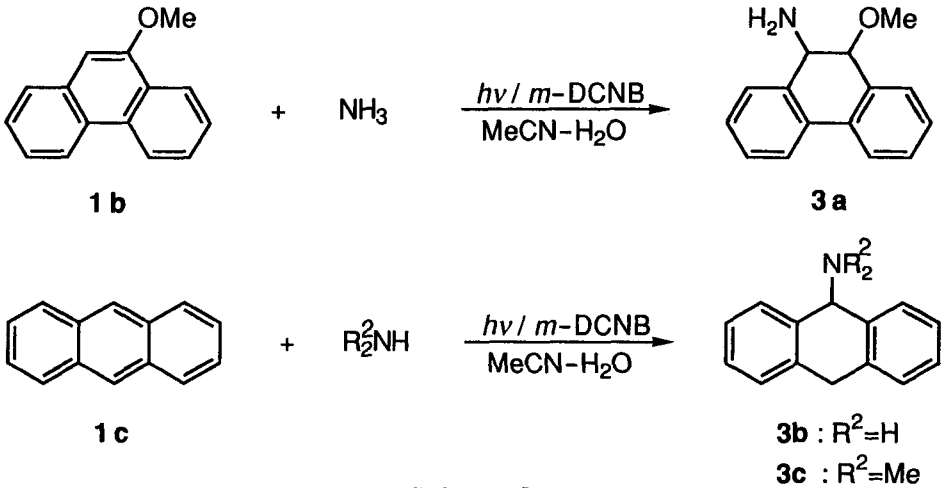
Table 1. Photoamination of Phenanthrene (**1a**) with Ammonia or Primary Amine[a]

Run No.	RNH_2	Irradn time / h	Product (Yield[b] / %)	Conv. of **1a** / %	Recov. of *m*-DCNB / %
1	NH_3	17	**2a** (84)	88	97
2[c]	NH_3	17	**2a** (0)	25	-
3[d]	NH_3	17	**2a** (64)	74	100
4	$MeNH_2$	12	**2b** (82)	74	92
5	$EtNH_2$	12	**2c** (95)	76	83
6[c]	$EtNH_2$	12	**2c** (0)	10	-
7	*i*-$PrNH_2$	12	**2d** (88)	74	66
8	*t*-$BuNH_2$	12	**2e** (88)	69	73
9	$PhCH_2NH_2$	16	**2f** (73)	62	96
10	$PhCH_2CH_2NH_2$	22	**2g** (78)	71	94
11	$CH_2{=}CHCH_2NH_2$	12	**2e** (85)	79	35
14	$NCCH_2CH_2NH_2$	14	**2g** (66)	71	57
13	$HOCH_2CH_2NH_2$	24	**2d** (82)	76	40
14	$H_2NCH_2CH_2NH_2$	15	**2f** (95)	58	67
15	$AcNHCH_2CH_2NH_2$	18	**1l** (66)	60	63
16	$EtOCOCH_2NH_2$	16	**2h** (78)	59	94

[a] For 140 mL of a 9:1 acetonitrile-water solutions containing **1a** (14 mmol), *m*-DCNB (3.5 mmol), and ammonia or an amine (140-350 mmol). [b] Isolated yields based on consumed **1a**. [c] In the absence of *m*-DCNB. [d] In dry acetonitrile solutions.

The photoamination of **1a** with ammonia or primary amines was thus carried out by irradiating a deaerated 9:1 (V:V) acetonitrile-water solution containing **1a**, *m*-DCNB, and ammonia or a primary amine by a high-pressure mercury arc at room temperature. As is shown in Table 1 and Scheme 2, photoamination was successfully achieved with ammonia and a wide variety of primary amines and gave selectively 9-amino- or 9-(alkylamino)-9,10-dihydrophenathrenes **2a-n** in fairly good yields, whereas *m*-DCNB was mostly recovered except in a few cases. For synthetic purpose, it is particularly significant that bifunctional alkylamines containing the vinyl, cyano, hydroxy, acetylamino and ethoxycarbonyl groups can be efficiently used as amination reagents that do not react with the other functional groups at all. It was confirmed that no reaction occurs at all in the dark nor even upon extensive irradiation in the absence of *m*-DCNB (runs 2 and 6).

Photoamination of Arenes with Ammonia. Similarly, photoamination with ammonia can be successfully applied to various arenes including 9-methoxyphenanthrene, anthracene, substituted naphthalenes, and a few benzene derivatives as shown in Table 2. Both 9-methoxyphenanthrene (**1b**) and anthracene (**1c**) were selectively photoaminated to give the corresponding 9-amino-9,10-dihydroarenes in good yields. Similarly, selective photoamination occurred with 2,3-dimethylnaphthalene (**1f**) and 2-methoxynapthalene (**1g**) to yield 1-amino-1,4-dihydronaphthalenes **3f** and **3g**, while both the corresponding 1-amino-1,4-



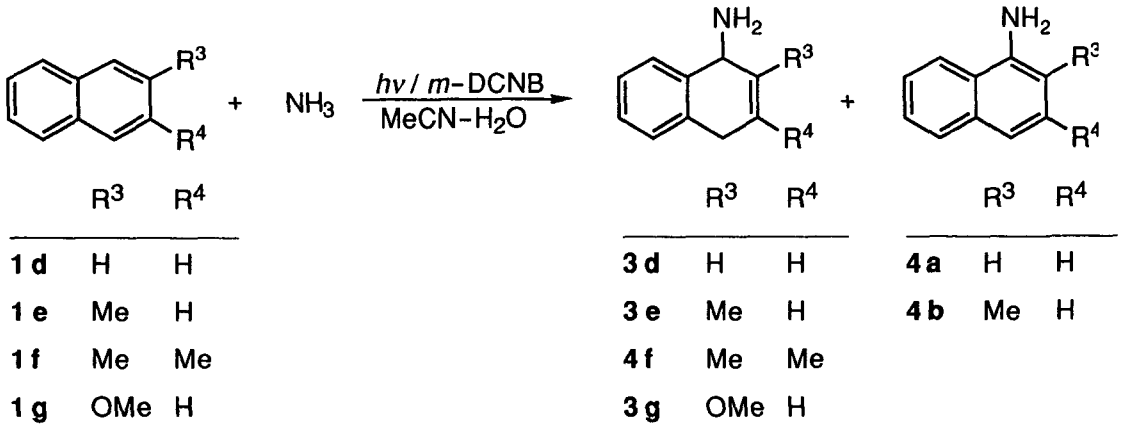
Scheme 3.

Table 2. Photoamination of Arenes with Ammonia[a]

Run No.	1	A[b]	Irradn. time / h	Products (Yield[c] / %)	Conv. of 1 / %	Recov. of A / %
1	**1b**	*m*-DCNB	2	**3a** (99)	95	83
2	**1c**	*m*-DCNB	18	**3b** (88)	82[d]	100
3	**1d**	*m*-DCNB	20	**3d** (48) **4a** (13)	79	100
4	**1e**	*m*-DCNB	15	**3e** (36) **4b** (19)	76	87
5	**1f**	*m*-DCNB	10	**3f** (81)	81	99
6	**1g**	*m*-DCNB	7	**3g** (75)	92	100
7	**1h**	*m*-DCNB	10	**3h** (15) **3i** (39) **3j** (23)	88	90
8	**1i**	*m*-DCNB	12	**3k** (26) **3l** (24) **4c** (19)	74	98
9	**1j**	*m*-DCNB	10	**3m** (19) **4a** (23) **5** (12) **6** (20)	63	93
10[e]	**1j**	none	10	**4a** (21)	9	-
11	**1k**	*m*-DCNB	7	**3n** (11) **4a** (24) **1d** (3)	38	97
12[e]	**1k**	none	7	**1d** (8)	11	-
13	**1l**	CNN	20	**4d** (41) **4e** (17)	31	51
14[f]	**1m**	DCNA	20	**4f** (43) **4g** (13)	25	*g*

[a] For 140 mL of 9:1 acetonitrile-water solutions containing arenes (14 mmol), an electron acceptor (A), and ammonia (350 mmol). In run 2, smaller amounts of **1c** (3 mmol) and *m*-DCNB (1.5 mmol) were used because of low silubility of **1c**. [b] Electron acceptor: *m*-DCNB = *m*-dicyanobenzene, CNN = 1-cyanonaphthalene, and DCNA = 9,10-dicyanoanthracene. *m*-DCNB, CNN, and DCNA were used in the amounts 3.5, 3.5, and 1.4×10^{-4} mmol, respectively. [c] Isolated yields based on consumed arenes. [d] Anthracene was recovered as photodimer. [e] In the absence of *m*-DCNB. [f] Under oxygen atomosphere. [g] Not determined.

dihydronaphthalenes (**3d** and **3e**) and 1-naphthylamines (**4a** and **4b**) were formed from naphthalene (**1d**) and 2-methylnaphthalene (**1e**) (Scheme 3). On the other hand, photoamination of the other naphthalene derivatives gave mixtures of aminated products, which are shown in Chart 1. The products were separated by column chromatography of their acetylated compounds on silica gel and were characterized by extensive NMR analysis involving spin decoupling as well as lanthanoid-induced shifts.



	R^3	R^4
1d	H	H
1e	Me	H
1f	Me	Me
1g	OMe	H

	R^3	R^4
3d	H	H
3e	Me	H
4f	Me	Me
3g	OMe	H

	R^3	R^4
4a	H	H
4b	Me	H

Scheme 3.

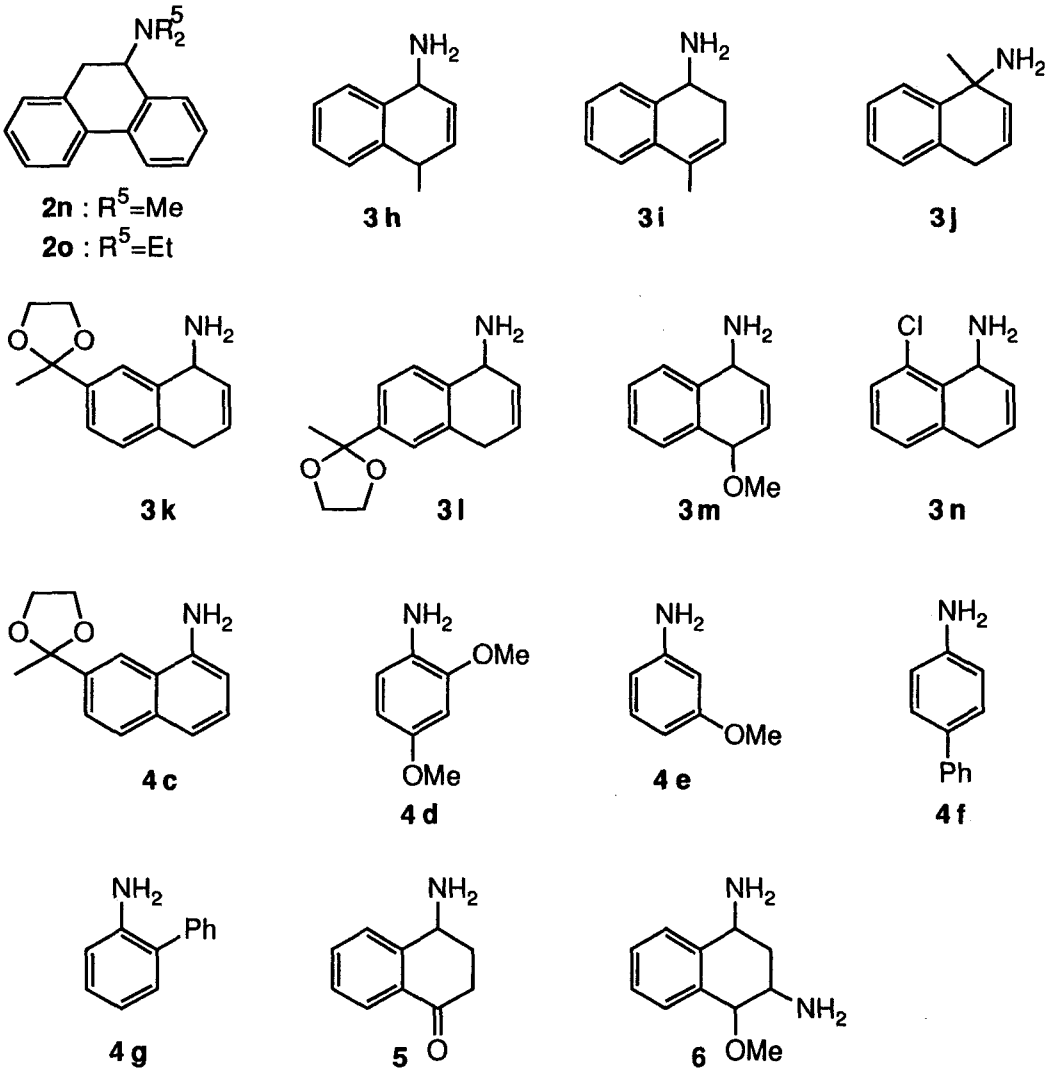


Chart 1.

Although irradiation of these naphthalene compounds in the absence of *m*-DCNB resulted in virtually no reaction with ammonia, 1-methoxynaphthalene (**1j**) reacted photochemically with ammonia in the absence of *m*-DCNB even in a low efficiency to give **4a**. In the case of 1-chloronaphthalene (**1k**), only dechlorination occurred in the absence of *m*-DCNB to give naphthalene. It is, however, evident that *m*-DCNB is requisite for efficient photoamination. The irradiation of **1j** in the presence of *m*-DCNB thus gave 1-amino-4-methoxy-1,4-dihydronaphthalene (**3m**), **4a**, 4-amino-1-tetralone (**5**), and 1,3-diamino-4-methoxytetralin (**6**), whereas the photoamination of **1k** resulted in the formation of 1-amino-8-chloro-1,4-dihydronaphthalene (**3n**) along with dechlorination products, **4a** and **1d**.

The photoamination of *m*-dimethoxybenzene (**1l**) can be carried out efficiently when CNN is used as the electron acceptor, thus giving 2,4-dimethoxyaniline (**4d**) and 3-methoxyanilin (**4e**), although this reaction is inefficient when *m*-DCNB is used as the electron acceptor. Although **1m** is not photoaminated at all under deaerated conditions, the photoamination under oxygen atmosphere gave 4- and 2-aminobiphenyl (**4f** and **4g**) in the presnce of DCNA.

Photoamination with Secondary Amines. Table 3 shows results of the photoamination of **1a** and **1c** with such secondary amines as dimethylamine and diethylamine. Although the presence of *m*-DCNB facilitated photoamination of either **1a** or **1c**, the efficiency of the photoamination of **1a** in this case is much lower than with ammonia and primary amines. Moreover, *m*-DCNB was substantially consumed during the photoreaction to give untractable materials from which 1-methyl- or 1-ethyl-2,4-dicyanobenzene (**9a** and **9b**) was isolated. On the other hand, the photoamination of anthracene with dimethylamine in the presence of *m*-DCNB occurred efficiently to give 9-(dimethylamino)-9,10-dihydroanthracene (**3c**) in 74 % yield. Although it was reported that **1c** can be directly photoaminated by aliphatic and aromatic secondary amines in the absence of an extra electron acceptor,[6] we found that the photoreaction of **1c** with dimethylamine in the absence of *m*-DCNB gave **3c** in only 8% yield and afforded anthracene photodimer (**8**) as the major product.

The photoamination reaction has thus been shown to be applicable to the efficient, direct amination of various arenes using ammonia and unactiveted alkylamines. The reaction conditions are so mild that this method can be successfully used for the direct introduction of various bifunctional amines. It is of synthetic interest to note that ethanolamine and alkylamine selectively react at the amino group, perhaps because of the much higher nucleophilicity of the amino group toward the aromatic cation radical compared with the hydroxy or olefinic group.

Table 3. Photoamination of Phenanthrene (**1a**) and Anthracene (**1c**) with Secondary Amines[a]

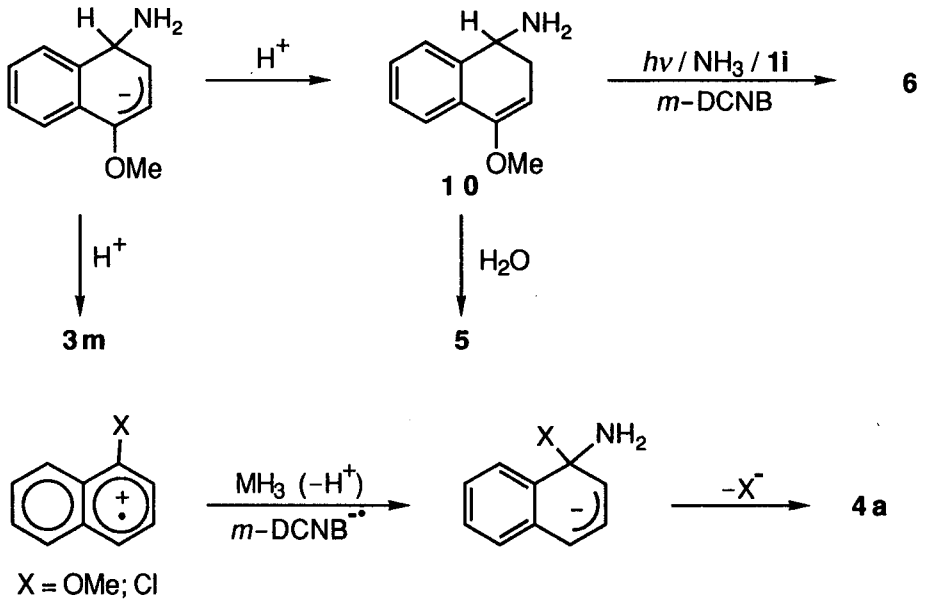
Run No.	**1**	R_2NH	Irradn. time / h	Products[b] (Yield[c] / %)	Conv. of **1** / %	Recov. of A[d] / %
1	**1a**	Me_2NH	50	**2n** (40) **7a** (3) **9a** (25)	55	29
2[e]	**1a**	Me_2NH	50	**2n** (7) **7a** (15)	54	-
3	**1a**	Et_2NH	50	**2o** (26) **7a** (6) **9b** (2)	31	49
4	**1c**	Me_2NH	2	**3c** (73) **7b** (11) **8** (4)	96	98
5[e]	**1c**	Me_2NH	2	**3c** (8) **7b** (18) **8** (74)	98	-

[a] For 140 mL of 9:1 acetonitrile-water solutions containing **1a** (7 mmol), an amine (28 mmol), and *m*-DCNB (14 mmol) in runs 1-3 or **1c** (2.8 mmol), dimethylamine (14 mmol), and *m*-DCNB (21 mmol) in runs 4 and 5. [b] Products: **7a** = 9,10-dihydrophenanthrene; **7b** = 9,10-dihydroanthracene; **8** = anthracene photodimer. [c] Isolated yields based on used **1** or *m*-DCNB. [d] A: Electron acceptor = *m*-dicyanobenzene. [e] In the absence of *m*-DCNB.

As has been discussed earlier, this facile photoamination is initiated by photoinduced electron transfer from the arene to the electron acceptor[2a-c,7] followed by nucleophilic attack of ammonia and primary amines on the aromatic cation radicals (Scheme 1). The one-electron reduction of the aminated neutral radicals by the anion radical of the electron acceptor gives rise to the final products after protonation. Therefore, the amination sites of the arenes should depend on population densities of the positive charge in cation radical molecules; this is in accord with the selective aminations of **1a**, **1b**, and **1c** at C-9 and the naphthalene compounds **1d-g**, at C-1. In the cases of **1h** and **1j**, moreover, nucleophilic attack of ammonia occurs at the both C-1 and C-4 positions of the cation radical, which suggests that positive charge density

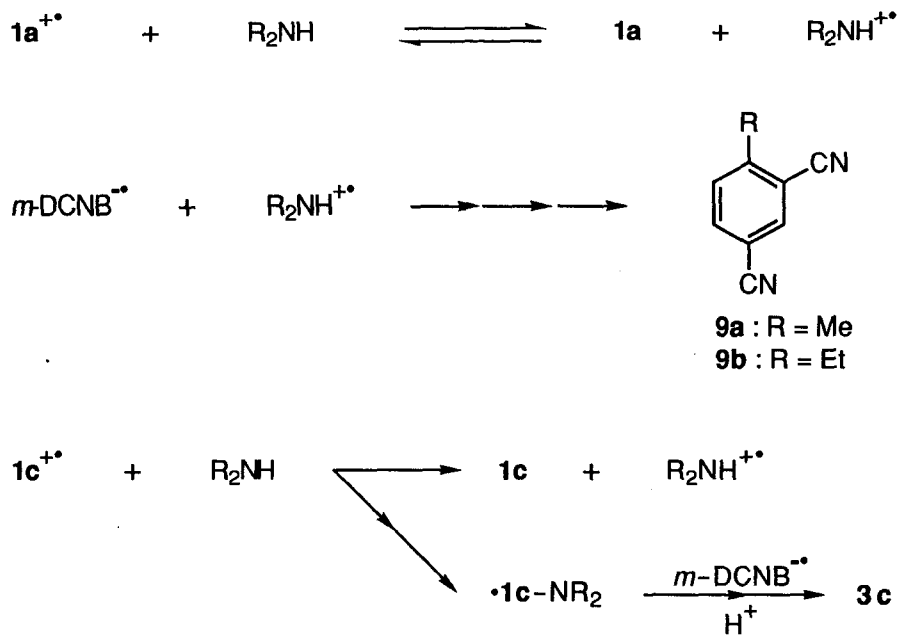
is essential in the regiochemistry of photoamination. On the other hands, the photoaddition of ammonia to **1i** shows that steric effects should also be taken into account.

The formation of **5** and **6** from the photoreaction of **1j** probably arises from hydrolysis and further photoamination, respectively, of an intermediate product **10**. Since **10** is a very electron-rich olefin, the cation radical of **1j** might efficiently undergo electron exchange with **10**[2c] to genarate the cation radical of **10**, which reacts with ammonia. The substitution product **4a** in the photoamination of **1j** and **1k** might be formed by nucleophilic attack at C-1 of the cation radicals followed by electron transfer from the anion radical of *m*-DCNB, since the chloride or methoxide anion is a better leaving group than the amino group (Scheme 4).



Scheme 4.

The photoaminations of **1a** with such secondary amines as dimethylamine or diethylamine are inefficient and accompanied by substantial consumption of *m*-DCNB. In contrast, **1c** was efficiently and cleanly photoaminated by the secondary amines along with the high-yield recovery of *m*-DCNB. The reactivity difference between **1a** and **1c** in the photoamination with the secondary amines might be associated with the lower oxidation potential of **1c** compared with that of **1a** (Scheme 5).[8]



Scheme 5.

2-1-3 Experimental

Photoamination of Arenes. General Procedures. In 140 mL of 9:1 (V:V) acetonitrile-water was dissolved a mixture of an arene (14 mmol), an electron acceptor (3.5 mmol), and an amine (140-350 mmol), and then solution was bubbled with argon for 20 min. In the case of such volatile amines as methylamine and ethylamine, each aqueous solution of the amine was added to a solution of an arene and an electron acceptor after argon bubbling, whereas ammonia solution was obtained by dissolving gaseous ammonia into argon-bubbled 9:1 (V:V) acetonitrile-water solution containing ArH, and an electron acceptor. The photoamination under an oxygen atmosphere was carried out after the solution had been bubbled with oxygen in place of argon. The soutions were irradiated with an Eikosha PIH-300 high-pressure mercury lamp through Pyrex under cooling with water. After evaporation under reduced pressure, the photolysates were dissolved in 150 mL of benzene and then extracted with dilute HCl. The acidic aqueous layer was basified with saturated $NaHCO_3$ followed by extraction with diethyl ether. Evaporation of the ether left crude aminated products. The starting arenes and electron acceptor were recovered from benzene solution. In some cases, the aminated products were acetylated with acetic anhydride in pyridine and then the acetylated compounds were

chromatographed on silica gel (Merck Art. No. 9385, 230-400 mesh) with hexane, benzene, and ethyl acetate as the eluents; the products were thus isolated. Irradiation times, yields of the products, recovered yields of the electron acceptor, and conversions of the arenes are listed in Table 1-3.

*9-Amino-9,10-dihydrophenanthrene (**2a**)*: ^{1}H NMR (CCl_4) δ = 1.8 (2H, br s), 2.6-3.3 (2H, m), 3.9-4.1 (1H, m), 7.1-7.3 (6H, m), and 7.5-7.7 (2H, m); IR ($CHCl_3$) 3360 and 3300 cm^{-1}; MS (CI method), *m/z* 195 (M^++1) and 178 (M^+-NH_3). The acetamide: Mp 155.5-156.5 °C (from methanol); Found: C, 81.09; H, 6.42; N, 5.87 %. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90 %.

*N-Methyl-9-amino-9,10-dihydrophenanthrene (**2b**)*: ^{1}H NMR (CCl_4) δ = 1.2 (1H, br s), 2.23 (3H, s), 2.92-3.00 (2H, m), 3.5 (1H, t, *J* = 5 Hz), 7.0-7.18 (6H, m), and 7.5-7.7 (2H, m); IR ($CHCl_3$) 3310 cm^{-1}; MS (CI method), *m/z* 252 (M^++1) and 178 (M^+-$NHCOCH_3$). The acetamide: Mp 121-122 °C (from methanol); Found: C, 81,39; H, 6.80; N, 5.62 %. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57 %.

*N-Ethyl-9-amino-9,10-dihydrophenanthrene (**2c**)*: ^{1}H NMR (CCl_4) δ = 0.86 (3H, *J* = 7 Hz, t), 1.03 (1H, br s), 2.5 (2H, q, *J* = 7 Hz), 2.86-2.96 (2H, m), 3.6 (1H, t, *J* = 5 Hz), 7.0-7.2 (6H, m), and 7.3-7.5(2H, m); IR ($CHCl_3$) 3310 cm^{-1}; MS (CI method), *m/z* 266 (M^++1) and 179 (M^+-N(COMe)Et). The acetamide: Mp 130.5-131.5 °C (from methanol); Found: C, 81.37; H, 7.13; N, 5.23 %. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28 %.

*N-Isopropyl-9-amino-9,10-dihydrophenanthrene (**2d**)*: ^{1}H NMR (CCl_4) δ = 1.80 (3H, d, *J* = 7.9 Hz,), 1.90 (1H, br s), 2.0 (3H, d, *J* = 6 Hz), 2.73 (1H, m), 2.87-2.92 (2H, m), 3.73(3H, t, *J* = 5 Hz), 7.0-7.2(6H, m), and 7.46-7.64(2H, m); IR ($CHCl_3$) 3310 cm^{-1}; MS (CI method), *m/z* 280 (M^++1) and 179 (M^+-N(COMe)-*i*-Pr). The acetamide: Mp 144.5-145.0 °C (from methanol); Found: C, 81.51; H, 7.55; N, 4.84 %. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01 %.

*N-tert-Butyl-9-amino-9,10-dihydrophenanthrene (**2e**)*: Mp 73-74 °C (from methanol); ^{1}H NMR (CCl_4) δ = 0.83 (1H, br s), 1.13 (9H, s), 2.73-2.89 (2H, m), 3.76-3.96 (1H, dd, *J* = 5 and 8 Hz), 7.0-7.23 (6H, m), and 7.33-7.66 (2H, m); IR ($CHCl_3$) 3310 cm^{-1}; MS, *m/z*

251 (M^+), 263 (M^+-Me), 194 (M^+-C_4H_9), and 178 (M^+-$C_4H_9NH_2$); Found: C, 85.77; H, 8.41; N, 5.44 %. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.77 %.

N-Benzyl-9-amino-9,10-dihydrophenanthrene (2f): ^1H NMR (CCl_4) δ = 1.36 (1H, br s), 2.87-3.00 (2H, m), 3.50-3.70 (3H, m), 6.93-7.11 (11H, m), and 7.4-7.6 (2H, m); IR ($CHCl_3$) 3310 cm^{-1}; MS, *m/z* 285 (M^+), 194 (M^+-CH_2Ph), and 178 (M^+-NH_2CH_2Ph). The acetamide: Mp 117-118 °C (from methanol); Found: C, 84.19; H, 6.38; N, 4.21 %. Calcd for $C_{27}H_{23}NO$: C, 84.37; H, 6.47; N, 4,28 %.

N-(2-Phenylethyl)-9-amino-9,10-dihydrophenanthrene (2g): ^1H NMR (CCl_4) δ = 0.92 (1H, br s), 2.53-2.69 (4H, m), 2.79-2.94 (2H, m), 3.50-3.69 (1H, m), 6.83-7.03 (11H, m), and 7.36-7.56 (2H, m); IR ($CHCl_3$) 3310 cm^{-1}; MS, *m/z* 299 (M^+) and 178 (M^+-$NH_2CH_2CH_2Ph$). The benzamide was obtained by a reaction of **2g** with benzoly chloride and K_2CO_3 in ether and water, Mp 126-127.5 °C (from methanol); Found: C, 85.94; H, 5.89; N, 3.44 %. Calcd for $C_{29}H_{25}NO$: C, 86.32; H, 6.25; N, 3.47 %.

N-Allyl-9-amino-9,10-dihydrophenanthrene (2h): ^1H NMR (CCl_4) δ = 1.36 (1H, br s), 2.8-3.1 (4H, m), 3.67 (1H, t, *J* = 5 Hz), 4.8-5.27 (2H, m), 5.4-5.9 (1H, m), 7.0-7.2 (6H, m), and 7.5-7.7(2H, m); IR (CCl_4) 3310 cm^{-1}; MS, *m/z* 235 (M^+), 194 (M^+-C_3H_5) and 178 (M^+-$NH_2C_3H_5$). The acetamide: Mp 130-131 °C (from methanol); Found: C, 82.03; H, 6.71; N, 5.03 %. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.98; N, 5.05 %.

N-(2-Cyanoethyl)-9-amino-9,10-dihydrophenanthrene (2i): ^1H NMR (CCl_4) δ = 2.30 (2H, m), 2.85 (3H, s), 3.17 (2H, t, *J* = 6.9 and 7.7 Hz), 3.86 (1H, t, *J* = 7.9 and 7.8 Hz), and 7.14-7.33 (10H, m); IR ($CHCl_3$) 1665 cm^{-1}; MS (CI method), *m/z* 253 (M^++1) and 222 (M^+-$NHCOCH_3$). The acetamide: Mp 60.0-61.0 °C (from methanol); Found: C, 80.65; H, 7.53; N, 5.79 %. Calcd for $C_{17}H_{19}NO$: C, 80.57; H, 7.56; N, 5.53 %.

N-(2-Hydroxyethyl)-9-amino-9,10-dihydrophenanthrene (2j): Mp 105-105.5 °C (from chloroform-ether); ^1H NMR (CCl_4) δ = 2.10 (2H, br s), 2.41-2.64 (2H, m), 2.96-3.05 (2H, m), 3.25-3.43 (2H, m), 3.66 (1H, t, *J* = 4 Hz), 7.0-7.2(6H, m), and 7.5-7.7(2H, m); IR ($CHCl_3$) 3400, and 3310 cm^{-1}; MS, *m/z* 239 (M^+), 193 (M^+-C_2H_6O), and 178 (M^+-

C_2H_7NO); Found: C, 79.93; H, 7.08; N, 5.87 %. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85 %.

*N-(2-Aminoethyl)-9-amino-9,10-dihydrophenanthrene (**2k**)*: ^{1}H NMR (CCl_4) δ = 1.1 (3H, br s), 2.58 (4H, s), 2.96-3.10 (2H, m), 3.7 (1H, t, J = 5 Hz), 7.0-7.2 (6H, m), and 7.5-7.7(2H, m); IR (CCl_4) 3400 cm^{-1}; MS, *m/z* 238 (M^+), 207 (M^+-CH_5N), and 178 (M^+-$C_2H_8N_2$). The dibenzamide: Mp 266-267 °C (from methanol); Found: C, 80.44; H, 5.75; N, 6.23 %. Calcd for $C_{30}H_{26}N_2O_2$: C, 80.69; H, 5.87; N, 6.27 %.

*N-(2-Acetamidoethyl)-9-amino-9,10-dihydrophenanthrene (**2l**)*: ^{1}H NMR (CCl_4) δ = 1.4 (1H, br s), 1.64 (3H, s), 2.43-2.60 (2H, m), 2.79-2.96 (4H, m), 3.56 (1H, t, J = 4 Hz), 6.17 (1H, br s), 6.92-7.24 (6H, m), and 7.36-7.56 (2H, m); IR ($CHCl_3$) 3440 and 1670 cm^{-1}; MS, *m/z* 280 (M^+), 208 (M^+-C_3C_6NO), 194 (M^+-C_4C_8NO) and 178 (M^+-$C_4C_{10}N_2O$). The benzamide: Mp 229-230 °C (from methanol); Found: C, 77,79; H, 6.22; N, 7.13 %. Calcd for $C_{25}H_{24}N_2O$: C, 78.10; H, 6.29; N, 7.29 %.

*N-((Ethoxycarbonyl)methyl)-9-amino-9,10-dihydrophenanthrene (**2m**)*: ^{1}H NMR (CCl_4) δ = 1.18 (3H, t, J = 7 Hz), 1.58 (1H, br s), 2.86-2.96 (2H, m), 3.17(2H, s), 3.70(1H, t, J = 5 Hz), 4.0(2H, q, J = 7 Hz), 7.0-7.2(6H, m). and 7.5-7.7(2H, m); IR ($CHCl_3$) 3320, and 1720 cm^{-1}; MS, *m/z* 281 (M^+), 178 (M^+-$C_4C_9NO_2$). The benzamide: Mp 183-183.5 °C (from ethanol); Found: C, 77.59; H, 5.96; N, 3.45 %. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63 %.

*N,N-Dimethyl-9-amino-9,10-dihydrophenanthrene (**2n**)*: ^{1}H NMR (CCl_4) δ = 2.83 (6H, s), 2.73-2.89 (2H, m), 3.53 (1H, t, J = 6 Hz), 6.86-7.20 (6H, m), and 7.26-7.53 (2H, m); MS, *m/z* 223 (M^+), 209 (M^+-CH_2) and 178 (M^+-C_2H_6N). The structure of **2n** was determined by comparison with an authentic sample prepared from methylation of **2b** with HCHO-HCO_2H according to the procedure of Wshweile-Clarke.[9)]

*N,N-Diethyl-9-amino-9,10-dihydrophenanthrene (**2o**)*: ^{1}H NMR (CCl_4) δ = 0.96 (6H, t, J = 7 Hz), 2.5 (4H, q, J = 7 Hz), 2.94-3.03 (2H, m), 3.69 (1H, t, J = 4 Hz), 7.0-7.2 (6H, m), and 7.46-7.73 (2H, m); MS *m/z* 251 (M^+), 223 (M^+-2×Me), 194 (M^+-2×Et), and 178

(M^+-NEt_2). The dehydrogenation of **2o** by Pd-C gave *N*, *N*-diethyl-9-amino-phenantherene.[10]

*9-Amino-10-methoxy-9,10-dihydrophenanthrene (**3a**)*: ^{1}H NMR ($CDCl_3$) δ = 1.69 (2H, br s), 3.36 (3H, s), 4.12 (1H, d, *J* = 4 Hz), 4.23 (1H, d, *J* = 4 Hz), 7.1-7.4 (6H, m), and 7.56-7.79 (2H, m); IR ($CHCl_3$) 3360 and 3300 cm^{-1}; MS, *m/z* 225 (M^+), 210 (M^+-Me), 193(M^+-MeOH) and 178(M^+-MeOH-NH_2). The acetamide: Mp 163.0-165.0 °C (from hexane-benzene); Found: C, 76.14; H, 6.30; N, 5.18 %. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24 %.

*9-Amino-9,10-dihydroanthracene (**3b**)*: ^{1}H NMR ($CDCl_3$) δ = 1.6 (2H, br s), 3.7-4.1 (2H, AB d, *J* = 18 Hz), 4.7 (1H, s), and 6.9-7.5 (8H, m); IR ($CHCl_3$) 3380 and 3310 cm^{-1}. The acetamide: Mp 206.5-207.0 °C (from benzene); MS (CI method), *m/z* 238 (M^++1) and 179 (M^++1 -NHCOMe); Found: C, 81.10; H, 6.39; N, 5.95 %. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90 %.

*N,N-Dimethyl-9-amino-9,10-dihydroanthracene (**3c**)*: Mp 67-69 °C (from benzene); ^{1}H NMR (CCl_4) δ = 2.0 (6H, s), 3.4-4.33 (2H, AB d, *J* = 16 Hz), 4.07 (1H, s), and 6.96-7.13 (8H, m); MS *m/z* 233 (M^+), 208 (M^+-Me), 193 (M^+-2×Me), 178 (M^+-$NHMe_2$). Compound **3c** was identified with an authetic sample prepared according to the reported method.[6]

*Photoamination of Naphthalene (**1d**) with Ammonia.* The aminated products were acetylated with Ac_2O-pyridine and then were chromatographed on silica gel with benzene-ethyl acetate (10:1) as eluent to afford the acetamide of **3d**. Further elution by benzene-ethyl acetate (4:1) gave the acetamide of **4a**.

The acetamide of **3d**: Mp 156.0-157.0 °C (from hexane-bnezene); ^{1}H NMR ($CDCl_3$, 360 MHz) δ = 2.02 (3H, s), 3.32-3.49 (2H, m), 5.7 (1H, br s), 5,75-5.81 (1H, m), 5.86-5.92 (1H, m), 6.07-6.12 (2H, m), 7.13-7.17 (1H, m), 7.21-7.29 (2H, m), and 7.38-7.43 (1H, m); IR ($CHCl_3$) 3440 and 1680 cm^{-1}. MS, *m/z* 187 (M^+), 144 (M^+-COMe) and 128 (M^+-NH_2COMe); Found: C, 76.93; H, 6.97; N, 7.44 %. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48 %.

The acetamide of **4a**: Mp 160.5-162 °C (from methanol). The acetamide of **4a** was unambiguously identified by direct comparison with an authentic sample.

*Photoamination of 2-Methylnaphthalene (**1e**).* The aminated products were acetylated with Ac_2O-pyridine and then were chromatographed on silica gel with benzene-ethyl acetate (10:1) as eluent to give the acetamides of **3e** and **4b**.

*The acetamide of **3e***: Mp 171-172.5 °C (from hexane-benzene); ^1H NMR ($CDCl_3$, 360 MHz) δ = 1.84 (3H, s), 2.00 (3H, s), 3.29-3.49 (2H, m), 5.58 (1H, br s), 5.67-5.73 (1H, m), 5.80-5.85 (1H, m), 7.12-7.15 (1H, m), 7.18-7.35 (2H, m), and 7.38-7.43 (1H, m); IR ($CHCl_3$) 3340 and 1660 cm^{-1}; MS, *m/z* 201 (M^+), 142 (M^+-NH_2COMe), and 140; Found: C, 77.29; H, 7.46; N, 6.91 %. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96 %. The acetamide of **3e** was converted into the acetamide of **4b** by refluxing a xylene solution in the presence of 5% Pd-C.

The acetamide of **4b**: Mp 195-196.5 °C (from hexane-benzene); ^1H NMR ($CDCl_3$, 360 MHz) δ = 1.63 (1H, s), 1.68 and 2.35 (3H, s), 2.26 and 2.43 (3H, s), and 7.18-7.86 (6H, m); IR ($CHCl_3$) 3440 and 1680 cm^{-1}; MS, *m/z* 199 (M^+); Found: C, 78.31; H, 6.56; N, 6.86 %. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03 %. The acetamide of **4b** was unambiguously identified by direct comparison with an authentic sample prepared by the acetylation of 2-methyl-1-aminonaphthalene.

*1-Amino-2,3-dimethyl-1,4-dihydronaphthalene (**3f**)*: ^1H NMR (CCl_4) δ = 1.29 (2H, br s), 1.62 (3H, s), 1.72 (3H, s), 3.02 (2H, br s), 3.83 (1H, br s), and 6.75-7.05 (4H, m); IR ($CHCl_3$) 3360 and 3300 cm^{-1}. The acetamide: Mp 201-202 °C (from methanol); ^1H NMR ($CDCl_3$) δ = 1.76 (6H, s), 1.92 (3H, s), 3.28 (2H, s), 5.58 (2H, br s), and 7.0-7.26 (4H, m); IR ($CHCl_3$) 3450 and 1660 cm^{-1}; MS, *m/z* 215 (M^+), 172 (M^+-COMe), and 156 (M^+-NH_2COMe); Found: C, 78.13; H, 7.98; N, 6.53 %. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51 %.

*1-Amino-2-methoxy-1,4-dihydronaphthalene (**3g**)*: ^1H NMR (CCl_4) δ = 2.59 (2H, br s), 2.33-2.46 (2H, m), 2.5 (3H, s), 4.13-4.33 (1H, m), 4.5-4.83 (1H, m), 6.92-7.10 (3H, m), and 7.33-7.59 (1H, m); IR ($CHCl_3$) 3360 and 3300 cm^{-1}. The acetamide: Mp 186-187

°C (from methanol); ^{1}H NMR ($CDCl_3$) δ = 1.98 (3H, s), 3.33-3.50 (2H, m), 3.53 (3H, s), 4.92 (1H, t, J = 4 Hz), 5.69 (2H, br s), and 7.0-7.2 (4H, m); IR ($CHCl_3$) 3470 and 1670 cm^{-1}; MS, *m/z* 217 (M^+), 174 (M^+-COMe), and 158 (M^+-NH_2COMe); Found: C, 71.83; H, 7.00; N, 6.46 %. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45 %.

*Photoamination of 1-Methylnaphthalene (**1h**) with Ammonia.* The aminated products were acetylated with Ac_2O-pyridine and then were chromatographed on silica gel with benzene-ethyl acetate (1:1) as eluent to give the acetamides of **3h**, **3i** and **3j**.

*The acetamide of **3h***: Mp 171-173 °C (from hexane-benzene); ^{1}H NMR ($CDCl_3$) δ = 1.3 (3H, d, J = 8 Hz), 1.9 (3H, s), 3.1-3.6 (1H, m), 5.4-6.2 (4H, m), and 7.0-7.3 (4H, m) ; IR ($CHCl_3$) 3430 and 1660 cm^{-1}; MS, *m/z* 201 (M^+), 186 (M^+-Me), 158 (M^+-COMe), 142 (M^+-NH_2COMe), and 128; Found: C, 77.40; H, 7.37; N, 6.84 %. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96 %.

*The acetamide of **3i***: Mp 190-192 °C (from hexane-benzene); ^{1}H NMR ($CDCl_3$) δ = 1.9 (3H, s), 2.1-2.2 (3H, m), 2.4-2.7 (2H, m), 5.0-5.4 (m, 1H), 5.6-6.1 (m, 2H), and 7.1-7.4 (m, 4H); IR ($CHCl_3$) 3440 and 1660 cm^{-1}; MS, *m/z* 201 (M^+), 186 (M^+-Me), 158 (M^+-COMe), 142 (M^+-NH_2COMe), 128; Found: C, 77.48; H, 7.21; N, 6.96 %. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96 %.

*The acetamide of **3j***: ^{1}H NMR ($CDCl_3$) δ = 1.6 (3H, s), 1.9 (3H, s), 3.35 (2H, br s), 5.7-6.1 (3H, m), and 7.0-7.4 (4H, m); IR ($CHCl_3$) 3450 and 1670 cm^{-1}; MS, *m/z* 201 (M^+), 186 (M^+-Me), 158 (M^+-COMe), 142 (M^+-NH_2COMe), and 128. Compound **3j** was crystallized as the benzamide: Mp 191-193°C (from hexane-benzene); ^{1}H NMR ($CDCl_3$) δ = 1.73 (3H, s), 3.46 (2H, br s), 5.96-6.07 (2H, m), 6.5 (1H, br s), and 7.06-7.76 (9H, m); Found: C, 81.63; H, 6.39; N, 5.18 %. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32 %.

*Photoamination of 2-Acetylnaphthalenen Ethylene Glycol Acetal (**1i**).* After the solvent had been evaporated, the residue was acetylated with Ac_2O-pyridine and then treated with 60% acetic acid in water at 50 °C for 3 h. The solution was extracted with benzene. After evaporation, the residue was chromatographed on silica gel with benzene-hexane to give 2-acethylnaphthalene and *m*-DCNB. Further elution with benzene-ethyl acetate gave *N*-acetyl-5-

amino-2-acetyl-5,8-dihydronaphthalene (**3k**), *N*-acetyl-8-amino-2-acetylnaphthalene (**3l**), and *N*-acetyl-8-amino-2-acetyl-5,8-dihydronaphthalene (**4c**).

*N-Acetyl-8-amino-2-acetyl-5,8-dihydronaphthalene (**3k**)*: Mp 163-164 °C (from hexane-ethylacetate); ^{1}H NMR ($CDCl_3$) δ = 2.0 (3H, s), 2.5 (3H, s), 3.3-3.5 (2H, m), 5.6-6.0 (4H, m), 7.1 (1H, d, J = 8 Hz), 7.6 (1H, d, J = 8 Hz), and 7.8 (1H, br s); IR ($CHCl_3$) 3430, 1680, and 1660 cm^{-1}; MS, *m/z* 229 (M^+), 186 (M^+-COMe), 170 (M^+-NH_2COMe), 155, 143, and 127; Found: C, 72.92; H, 6.54; N, 6.01 %. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11 %.

*N-Acetyl-5-amino-2-acetyl-5,8-dihydronaphthalene (**3l**)*: Mp 159-160 °C (from hexane-ethylacetate); ^{1}H NMR ($CDCl_3$) δ = 2.0 (3H, s), 2.5 (3H, s), 3.3-3.5 (2H, m), 5.6-6.2 (4H, m), 7.4 (1H, d, J = 8 Hz), 7.6 (1H, br s), and 7.6 (1H, d, J = 8 Hz); IR ($CHCl_3$) 3440, 1690, and 1665 cm^{-1}; MS, *m/z* 229 (M^+), 186 (M^+-COMe), 170 (M^+-NH_2COMe), 155, 144, and 127; Found: C, 73.00; H, 6.51; N, 6.02 %. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11 %.

*N-acetyl-8-amino-2-acetylnaphthalene (**4c**)*: Mp 199-200 °C (from hexane-ethhylacetate); ^{1}H NMR (CD_3COCD_3) δ = 1.6 (1H, br s), 2.2 (3H, s), 2.6 (3H, s), 7.4-7.6 (2H, m), 7.8-8.1 (3H, m), and 8.2 (1H, br s); IR (KBr) 3440, 1680, and 1665 cm^{-1}; MS, *m/z* 227 (M^+), 185 (M^+-$COCH_2$), 170 (M^+-NCOMe), 142, and 115; Found: C, 73.70; H, 5.65; N, 6.09 %. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16 %.

*The Photoamination of 1-Methoxynaphthalene (**1j**) with Ammonia.* After the solution was evaporated from the irradiated solutions, the residue was acetylated with Ac_2O-pyidine. The solvent was removed, and the residue was chromatographed on silica gel with benzene-ethyl acetate (4:1) as eluent to give the acetamide of **4a**. Further elution with benzene-ethyl acetate (1:1) gave the acetamide of **3m** and the acetamide of **5**. The diacetamide of **6** was obtained by elution with ethyl acetate-methanol (10:1).

*The acetamide of **3m***: Mp 156-159 °C (from hexane-benzene); ^{1}H NMR ($CDCl_3$) δ = 2.0 (3H, s), 3.1 (3H, s), 5.0-5.1 (1H, m), 5.6-5.8 (2H, m), 6.1-6.2 (2H, m), and 7.3-7.6 (4H, m); IR ($CHCl_3$) 3340 and 1660 cm^{-1}; MS, *m/z* 186 (M^+-OMe), 184, 158 (M^+-

H_2COMe), and 142 (M^+-HOMe -COMe); Found: C, 71.82; H, 6.91; N, 6.59 %. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45 %.

The acetamide of ***5***: Mp 145-146 °C (from hexane-benzene); ^1H NMR ($CDCl_3$) δ = 2.1 (3H, s), 2.2-2.4 (2H, m), 2.6-2.8 (2H, m), 5.1-5.5 (1H, m), 5.7-6.1 (1H, m), 7.3-7.5 (3H, m), and 7.8-8.0 (1H, m); IR ($CHCl_3$) 3440, 1690, and 1665 cm^{-1}; MS, *m/z* 203 (M^+), 160 (M^+-COMe), 144 (M^+-NH_2COMe), and 133; Found: C, 70.84; H, 6.45; N, 6.88 %. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89 %.

The acetamide of ***6***: Mp 274-275 °C (from ethylacetate-ethanol); ^1H NMR ($CDCl_3$, 360 MHz) δ = 1.78-1.85 (1H, m), 1.96 (3H, s), 2.06 (3H, s), 2.68-2.95 (1H, m), 3.30 (3H, s), 4.33-4.44 (1H, m), 4.53 (1H, d, J = 6.9 Hz), 5.05 (1H, dd, J = 7.3, 5.3 Hz), 6.21 (1H, br s), 6.50 (1H, br s), and 7.28-7.37 (4H, m); IR (KBr) 3280 and 1645 cm^{-1}; MS, *m/z* 276 (M^+), 245 (M^+-OMe), 217 (M^+-H_2NCOMe), 201, 191, 185, 158, 147, 143, 134, and 117; Found: C, 65.18; H, 7.18; N, 9.99 %. Calcd for $C_{15}H_{20}N_2O_3$: C, 65.19; H, 7.30; N, 10.14 %.

*Photoamination of 1-chloronaphthalene (****1k****).* The aminated products were acetylated with Ac_2O-pyridine and then chromatographed on silica gel with benzene-ethyl acetate (4:1) as eluent to give the acetamides of **4a** and **3n**.

The acetamide of ***3n***: Mp 225-226 °C (from hexane-benzene); ^1H NMR ($CDCl_3$) δ =1.9 (3H, s), 3.4-3.5 (2H, m), 5.4-5.8 (2H, m), 5.9-6.0 (2H, m), and 7.0-7.3 (3H, m); IR ($CHCl_3$) 3340 and 1670 cm^{-1}; MS, *m/z* 221 (M^+), 186 (M^+-Cl), 162 (M^+-NH_2COMe), 143, and 128; Found: C, 64.92; H, 5.44; N, 6.33, Cl, 15.69 %. Calcd for $C_{12}H_{12}NOCl$: C, 65.01; H, 5.46; N, 6.32, Cl, 15.99 %.

*Photoamination of m-dimethoxybenzene (****1l****).* The aminated products were asetylated with Ac_2O-pyridine and then chromatographed on silica gel with hexane-benzene (1:1) to give the acetamides of **4d** and **4e**.

The acetamide of ***4d***: Mp 118-120 °C (from benzene); ^1H NMR ($CDCl_3$) δ = 2.15 (3H, s), 3.75 (3H, s), 3.80 (3H, s), 6.25-6.6 (2H, m), 7.55 (1H, br s), and 8.0-8.3 (1H, m); IR

($CHCl_3$) 3450 and 1680 cm^{-1}; MS, *m/z* 195 (M^+), 137 (M^+-NHCOMe); Found: C, 61.43; H, 7.00; N, 7.13 %. Calcd for $C_{10}H_{13}NO_3$: C, 61.52; H, 6.71; N, 7.18 %.

The acetamide of ***4e***: ^1H NMR (CCl_4) δ = 2.05 (3H, s), 3.75 (3H, s), 6.5-7.0 (3H, m), 7.65 (1H, br s), and 8.1-8.4 (1H, m).

The structure of the acetamide of **4e** was determined by direct comparison with an authentic sample.

Photoamination of Biphenyl (**1m**). The aminated products were separated by chromatography on silica gel with hexane-benzene (1:1) as eluent. The structures of **4f** and **4g** were determined by direct comparison with an authentic samples. *Compound of **4f***: Mp 176-177 °C (for the acetamide; from benzene); ^1H NMR (CCl_4) δ = 3.40 (2H, br s), 6.25-6.70 (2H, m), and 6.9-7.7 (7H, m); IR 3480 and 3400 cm^{-1}. *Compound **4g***: ^1H NMR (CCl_4) δ = 3.56 (2H, br s), and 6.4-7.5 (9H, m); IR ($CHCl_3$) 3480 and 3400 cm^{-1}.

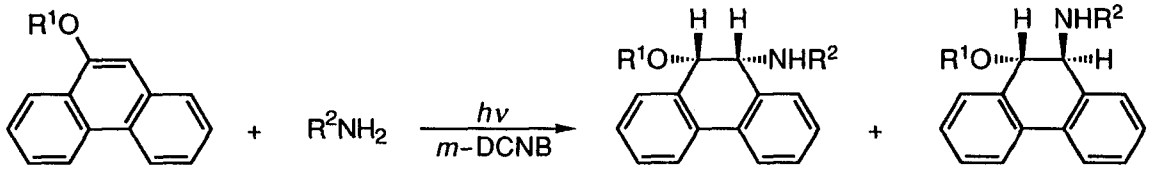
*1-Methyl-2,4-dicyanobenzene (**9a**)*: Mp 142-143 °C (from methanol); ^1H NMR (CCl_4) δ = 2.56 (3H, s), 7.36 (1H, d, *J* = 8 Hz), 7.66 (1H, dd, *J* = 8.02 Hz), and 7.76 (1H, m); IR ($CHCl_3$) 2250 cm^{-1}; MS, *m/z* 142 (M^+) and 115; Found: C, 75.84; H, 4.19; N, 19.61 %. Calcd for $C_9H_6N_2$: C, 76.04; H, 4.25; N, 19.71 %.

*1-Ethyl-2,4-dicyanobenzene (**9b**)*: ^1H NMR (CCl_4) δ = 1.33 (3H, t, *J* = 8 Hz), 2.96 (2H, q, *J* = 8 Hz), 7.30 (1H, d, *J* = 8 Hz), 7.63 (1H, dd, *J* = 8.2 Hz), and 7.76 (1H, m); IR ($CHCl_3$) 2250 cm^{-1}; MS, *m/z* 156 (M^+), 141 (M^+-Me), 127 (M^+ -Et), and 114.

2-2 Stereochemical Studies on Photoamination of Phenenthrene Derivatives with Ammonia and Alkylamines

2-2-1 Introduction

Photoaddition of nucleophiles to a variety of substrates via photoinduced electron transfer has been widely investigated from synthetic and mechanistic points of view.[11] The photoaddition provides a potentially useful synthetic procedure to achieve the introduction of functional groups into electron-rich substrates. However, few stereochemical studies on the photoaddition have been reported.[12-16] In Section 2-1, the author discussed an efficient photoamination using ammonia and primary amines as nucleophiles in order to establish synthetic scope and limitations. However, the stereochemistry of the addition of the amine is left undetermined. In this Section, the author wishes to report the stereochemistry of photoamination of some phenanthrene derivatives and anthracene.



1b : R^1 = Me
11 : R^1 = Et

a

b

13 : R^1 = Me; R^2 = H
14 : R^1 = Et; R^2 = H
15 : R^1 = Me; R^2 = *i*-Pr
16 : R^1 = Et; R^2 = *t*-Bu

Scheme 6.

2-1-2 Results and Discussion

Stereochemistry. Irradiation of a 9:1 (V:V) acetonitrile-water solution containing an arene (**1a-b** and **11-12**), *m*-dicyanobenzene (*m*-DCNB), and ammonia or primary alkylamines (*i.e.* propylamine, isopropylamine and *tert*-butylamine) with a high-pressure mercury lamp though a Pyrex filter gave the corresponding 9-amino- or 9-alkylamino-9,10-dihydroarenes **13-16**. The photoamination of 9-methoxyphenanthrene (**1b**) with ammonia gave *cis*- and *trans*-9-amino-10-

Table 4. Final atomic coordinates ($\times 10^3$) with their estimated standard deviations

Atom	x	y	z	Atom	x	y	z
O(1)	-47(0)	-70(1)	805(0)	C(8)	-104(1)	260(1)	705(3)
O(2)	223(1)	47(1)	1271(1)	C(9)	-21(1)	306(1)	668(3)
N(1)	145(1)	5(1)	1017(2)	C(10)	82(1)	270(1)	731(2)
C(1)	-161(1)	33(1)	908(2)	C(11)	103(1)	181(2)	833(2)
C(2)	-243(1)	-20(1)	946(2)	C(12)	18(1)	141(1)	871(2)
C(3)	-338(1)	32(2)	921(3)	C(13)	41(1)	53(1)	990(2)
C(4)	-355(1)	126(2)	860(2)	C(14)	-49(1)	-24(1)	942(2)
C(5)	-272(1)	178(1)	824(2)	C(15)	-106(1)	-161(1)	769(2)
C(6)	-175(1)	129(1)	850(2)	C(16)	218(1)	7(1)	1152(2)
C(7)	-85(1)	180(1)	805(2)	C(17)	319(1)	-61(2)	1153(3)

methoxy-9,10-dihydrophenanthrene (**13a, b**) in a ratio of 75:25 (Scheme 6). The structure of the major product was confirmed by X-ray crystallographic analysis; the acetamide of **13a** has a cis configuration with respect to the acetylamino and methoxy groups. Table 4 lists the final atomic parameters for the acetamide of **13a**, and Tables 5 and 6 list bond distances and bond angles. The crystal packing diagram and an ORTEP drawing are shown in Fig. 1. Naturally the structure of the minor product was found to be trans isomer **13b**.

Table 5. Bond distances of the acetamide of **13a**

Bond distances / Å					
O(1)-C(14)	1.38(2)	C(3)-C(4)	1.33(3)	C(11)-C(12)	1.41(2)
O(1)-C(15)	1.38(2)	C(4)-C(5)	1.41(3)	C(12)-C(13)	1.53(2)
O(2)-C(16)	1.19(2)	C(5)-C(6)	1.36(2)	C(13)-C(14)	1.49(2)
N(1)-C(13)	1.45(2)	C(6)-C(7)	1.53(2)	C(16)-C(17)	1.58(3)
N(1)-C(16)	1.28(2)	C(7)-C(8)	1.35(2)		
C(1)-C(2)	1.41(2)	C(7)-C(12)	1.37(2)		
C(1)-C(6)	1.34(2)	C(8)-C(9)	1.38(2)		
C(1)-C(14)	1.58(2)	C(9)-C(10)	1.35(3)		
C(2)-C(3)	1.37(3)	C(10)-C(11)	1.37(3)		

Table 6. Bond angles of the acetamide of **13a**

Bond angles / deg			
C(14)-O(1)-C(15)	114(1)	C(8)-C(9)-C(10)	119(2)
C(13)-N(1)-C(16)	120(1)	C(9)-C(10)-C(11)	120(2)
C(2)-C(1)-C(6)	122(1)	C(10)-C(11)-C(12)	120(2)
C(2)-C(1)-C(14)	117(2)	C(7)-C(12)-C(11)	118(2)
C(6)-C(1)-C(14)	121(1)	C(7)-C(12)-C(13)	121(2)
C(1)-C(2)-C(3)	117(2)	C(11)-C(12)-C(13)	121(2)
C(2)-C(2)-C(4)	122(2)	N(1)-C(13)-C(12)	113(1)
C(3)-C(4)-C(5)	121(2)	N(1)-C(13)-C(14)	111(1)
C(4)-C(5)-C(6)	119(2)	C(12)-C(13)-C(14)	110(1)
C(1)-C(6)-C(5)	120(2)	O(1)-C(14)-C(1)	109(1)
C(1)-C(6)-C(7)	119(2)	O(1)-C(14)-C(13)	108(1)
C(5)-C(6)-C(7)	121(2)	C(1)-C(14)-C(13)	109(1)
C(6)-C(7)-C(8)	122(2)	O(2)-C(16)-C(1)	134(2)
C(6)-C(7)-C(12)	117(2)	O(2)-C(16)-C(17)	116(2)
C(8)-C(7)-C(12)	121(2)	N(1)-C(16)-C(17)	110(2)
C(7)-C(8)-C(9)	122(2)		

The ^{1}H NMR spectrum [Fig. 2(a)] of a mixture of **13a, b** shows that a hydrogen (H^c) attached to the methoxyated carbon of **13a** (4.18 ppm) appeared at higher field than H^a of **13a** (4.26 ppm). This is clearly due to the substantial shielding effect of an amino group to a hydrogen (H^c) which is located in the *cis* position towards the amino group. In the ^{1}H NMR spectrum [Fig. 2(b)] of the acetamide of **13a, b**, the peak for H^c of the acetamide of **13b** shows a downfield shift of 0.18 ppm from that of parent **13b** whereas the peak for H^a of the acetamide of **13a** shows only a slight shift from parent of **13a**, thus indicating that the deshielding effect of the acetamide group operates effectively for a hydrogen (H^c) which is located in the cis postion to the acetamide group.

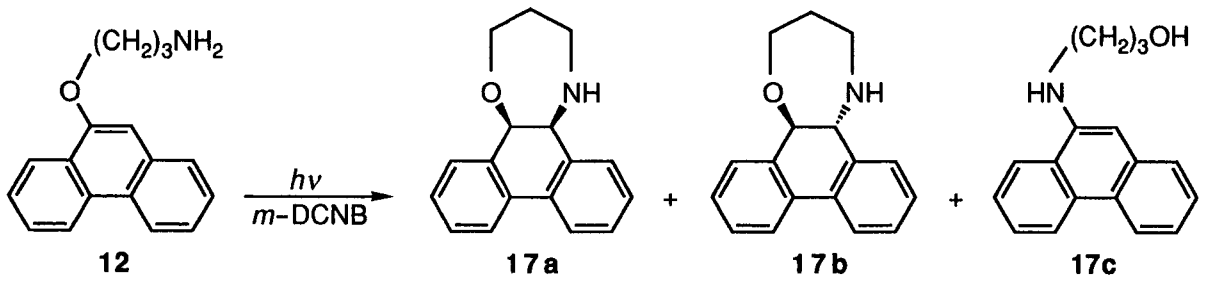
On the basis of these obserbations from ^{1}H NMR spectra, the configuration of aminated compounds **14-16** from 9-alkoxyphenanthrene **1a-b** and **11-12** was assigned by their ^{1}H NMR spectra (Figs. 3 and 4). Table 7 lists the isomer ratios determined from peak ratios for

methine protons at C-9 or C-10 in the ^1H NMR spectra as well as product yields. The photoamination of **11** with ammonia give *cis*- and *trans*-9-amino-10-ethoxy-9,10-dihydrophenanthrene (**14a,b**) in a ratio of 73:27. The photoamination of **1b** with isopropylamine and of **2** with *tert*-butylamine gave exclusively *cis*-9-(*N*-isopropylamino)-10-methoxy-9,10-dihydrophenanthrene (**15a**) and *cis*-9-(*N*-*tert*-butylamino)-10-ethoxy-9,10-dihydrophenanthrene (**16a**), respectively (Scheme 6). Intramolecular photoamination of 9-(3-aminopropoxy)-phenanthrene (**3**) gave phenanthro[9,10-*b*]-4-oxazepine derivatives (**17a, b**) in a trans to cis isomer ratio of 65:35, along with 3-[*N*-(9-phenanthryl)amino]propanol (**17c**) (Scheme 7).

Table 7. Photoamination of Arenes (**1a-c** and **11-12**) with Amines[a]

Run No.	RNH_2	Irradn. time / h	Product (**a** : **b**)[c]	Yield[b] / %	Conv. of Arene / %	Recov. of *m*-DCNB / %
1b	NH_3	2	**13** (75:25)	100	69	95
11	NH_3	5	**14** (73:27)	95	79	81
1b	*i*-$PrNH_2$	5	**15** (100:0)	99	92	80
11	*t*-$BuNH_2$	5	**16** (100:0)	81	76	83
12		1.5	**17** (65:35) **17c**	41 18	100	100
1a	ND_3	4	**18** (84:16)	86	68	80
1a-d_{10}	$PrNH_2$	10	**19** (17:83)	88	93	87
1c	ND_3	1.5	**20** (95:5)	64	87	100

[a] For an acetonitrile-H_2O (9:1) or acetonitrile-D_2O (9:1) solution (50 mL) containing an arene (2.5 mmol), *m*-DCNB (2.5 mmol), and RNH_2 (25 mmol). [b] Isolated yield based on consumed arene. [c] Isomer ratio of **a** to **b**.



Scheme 7.

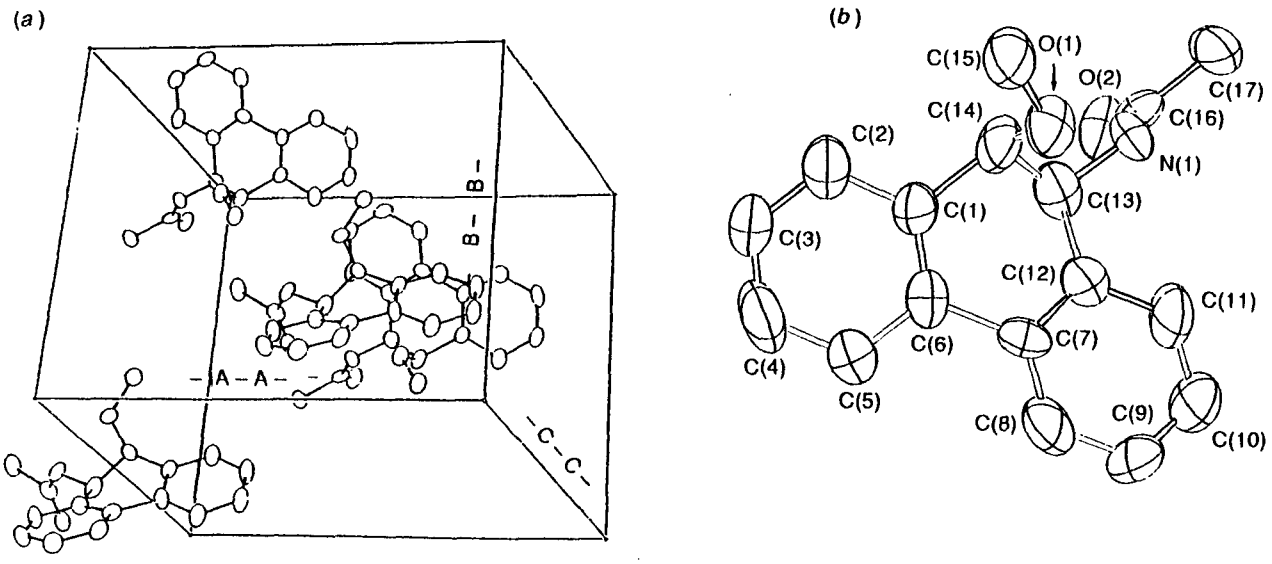
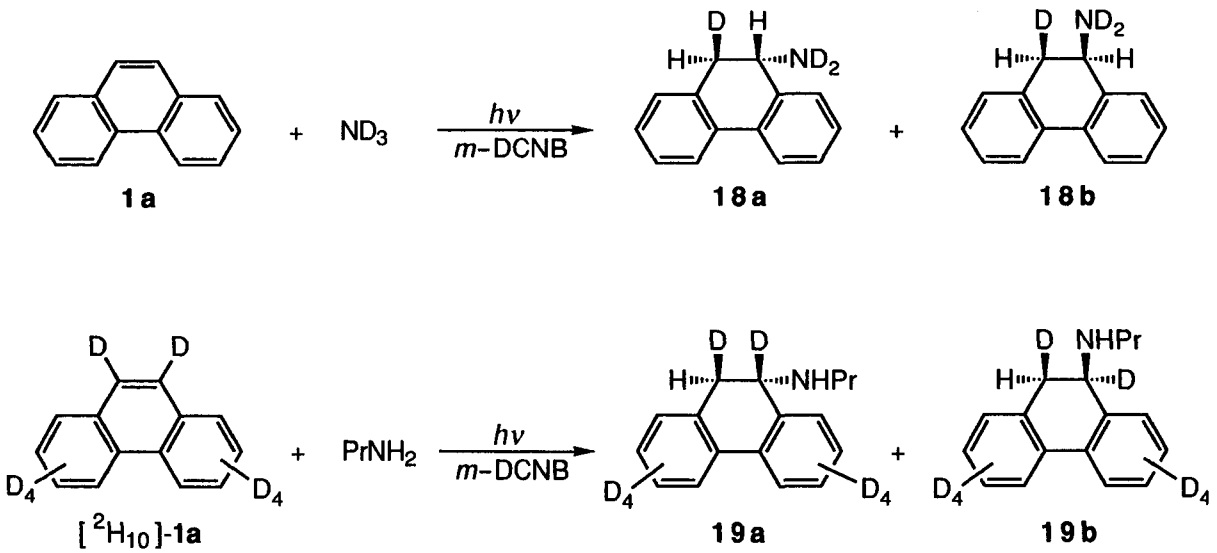
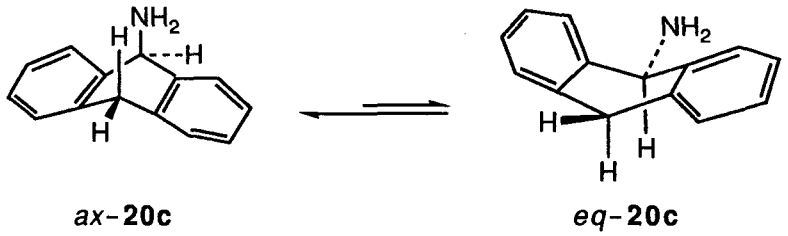


Fig. 1. (a) Crystal-packing diagram in unit cell and (b) an ORTEP drawing of the acetamide of **13a**. The numbering of carbon atom is performed independently to the text but corresponds to Tables 4 -6.

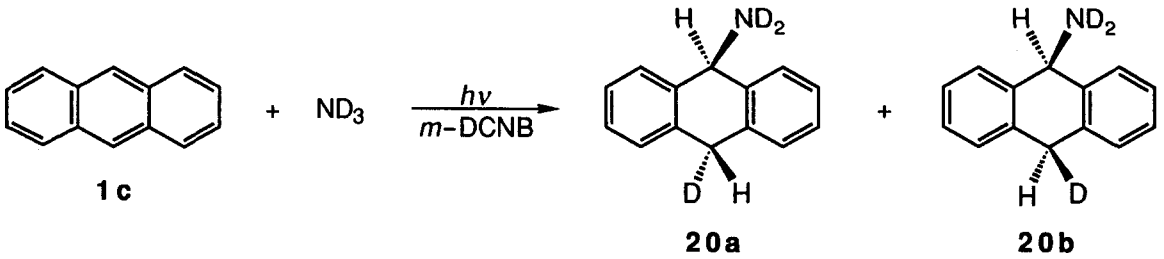
The stereochemistry of the photoamination of phenanthrene (**1a**) was studied using [$^2H_3$]ammonia in CH_3CN-D_2O; 9-(*N*,*N*-dideuterioamino)-10-deuterio-9,10-dihydrophenanthrene (**18a,b**) was formed (Scheme 8). In the ^1H NMR spectra [Fig. 5(c)] of 9-amino-9,10-dihydrophenanthrene (**18c**) formed by photoamination of **1a** with ammonia, the methylene protons (H^a and H^b) appear as two AB-type doublets of doublets, of which the peak at higher field can be assigned to the hydrogen (H^a) located at the cis position to the amino group. The ^1H NMR spectrum [Fig. 5(b)] of **18a,b** showed that deuterium was incorporated at C-10 in 90% yield and that a ratio of the cis to trans configuration between the amino group and the hydrogen on C-10 was 84:16. The photoamination of phenanthrene-d_{10} (**1a**-d_{10}) with propylamine gave 9-propyl-amino-9,10-dihydro-10-deuteriophenanthrene (**19a,b**), of which the amino group and the hydrogen on C-10 were arranged in cis and trans configurations in a ratio of 17:83 [Fig.5(a)]. Thus the addition of the amine and ammonia to the phenanthrene moiety occurred predominantly in a *trans* manner.



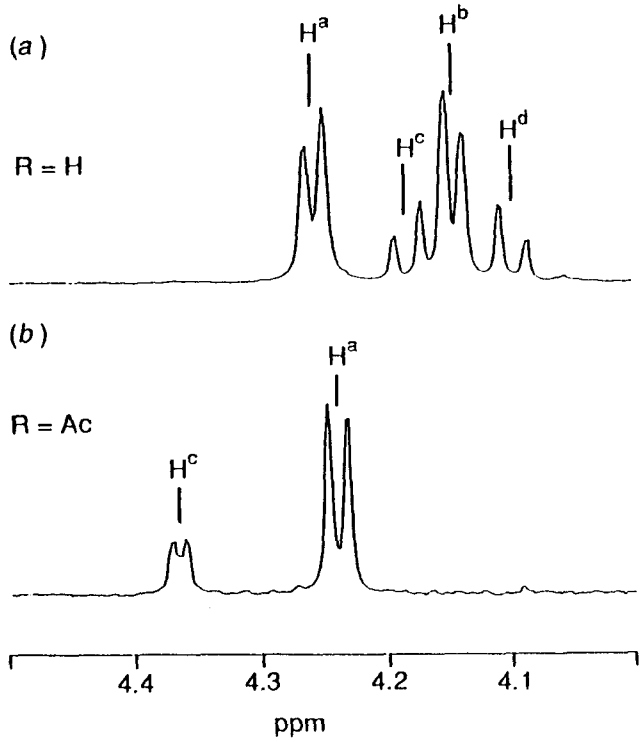
Scheme 8.

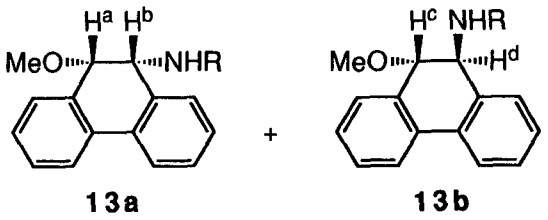


Scheme 9.



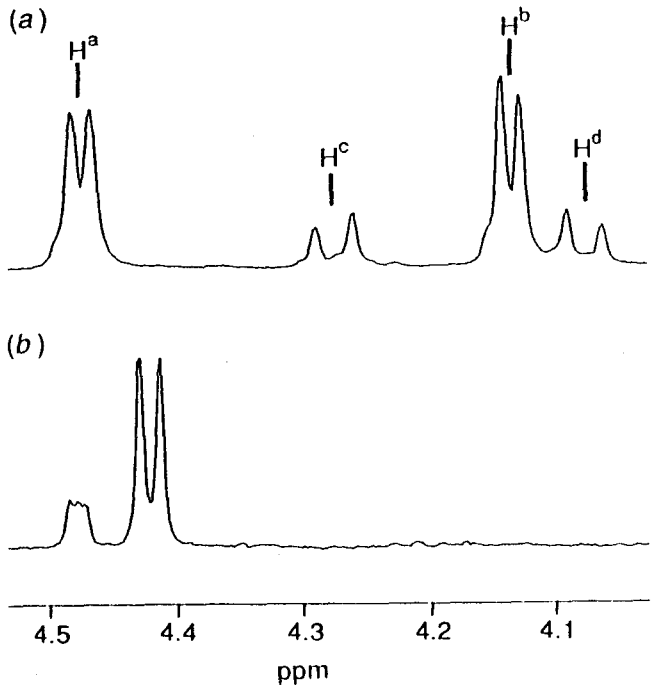
Scheme 10.

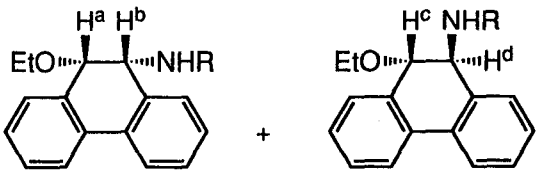




13a **13b**

Fig. 2. ^{1}H NMR spectra of (a) **13a** and **13b**, and (b) the acetamides of **13a** and **13b** in the 4.0-4.5 ppm region





14a **14b**

Fig. 3. ^{1}H NMR spectra of (a) **14a** and **14b**, and (b) the acetamides of **14a** and **14b** in the 4.0-4.6 ppm region

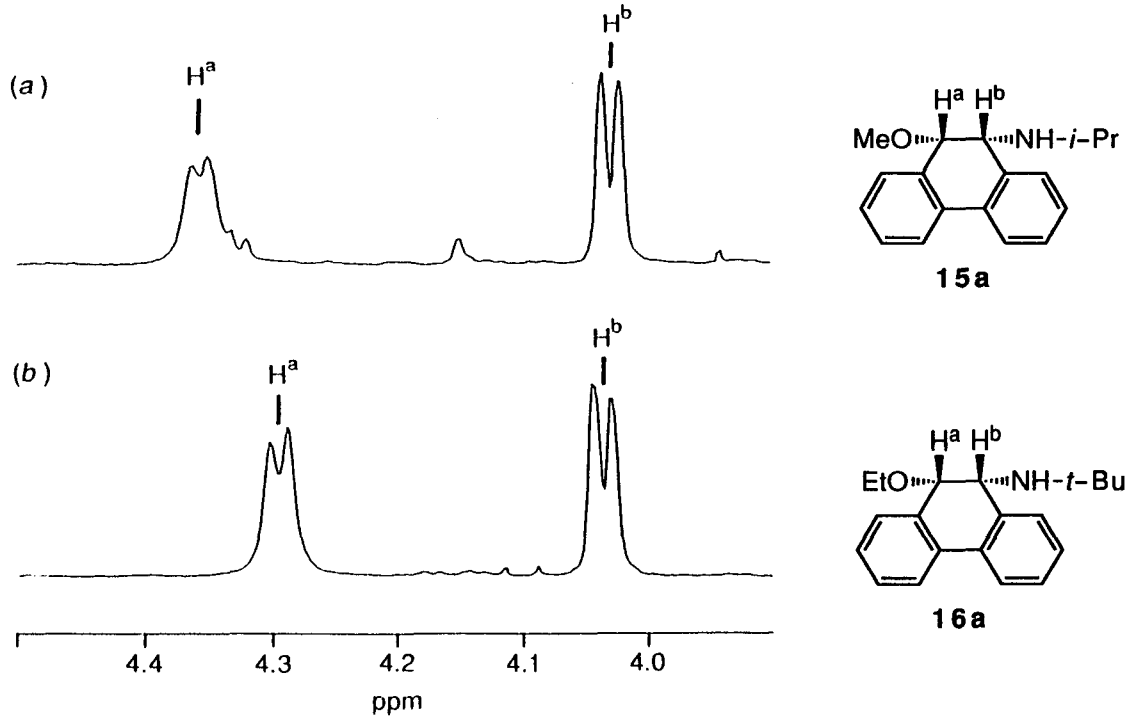


Fig. 4. ^{1}H NMR spectra of (a) **15a** and (b) **16a** in the 3.9-4.5 ppm region

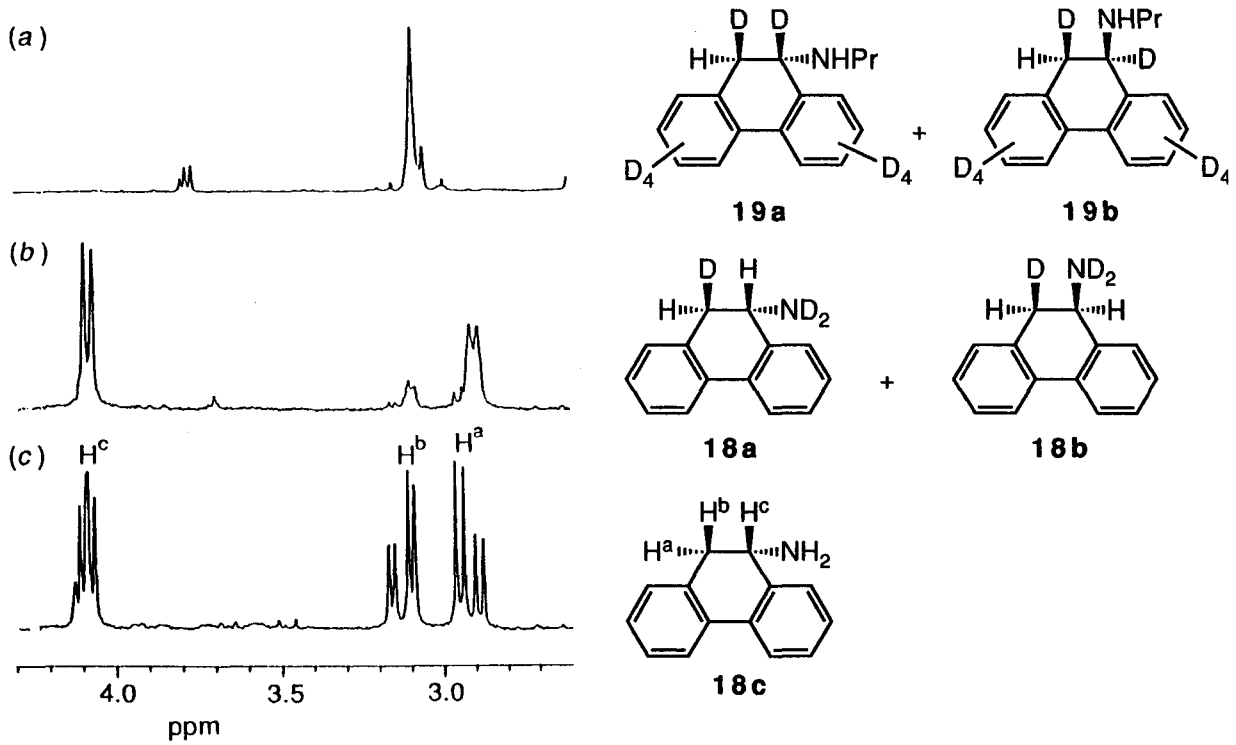


Fig. 5. ^{1}H NMR spectra of (a) **19a** and **19b**, (b) **18a** and **18b**, and (c) **18c** in the 2.6-4.3 ppm region

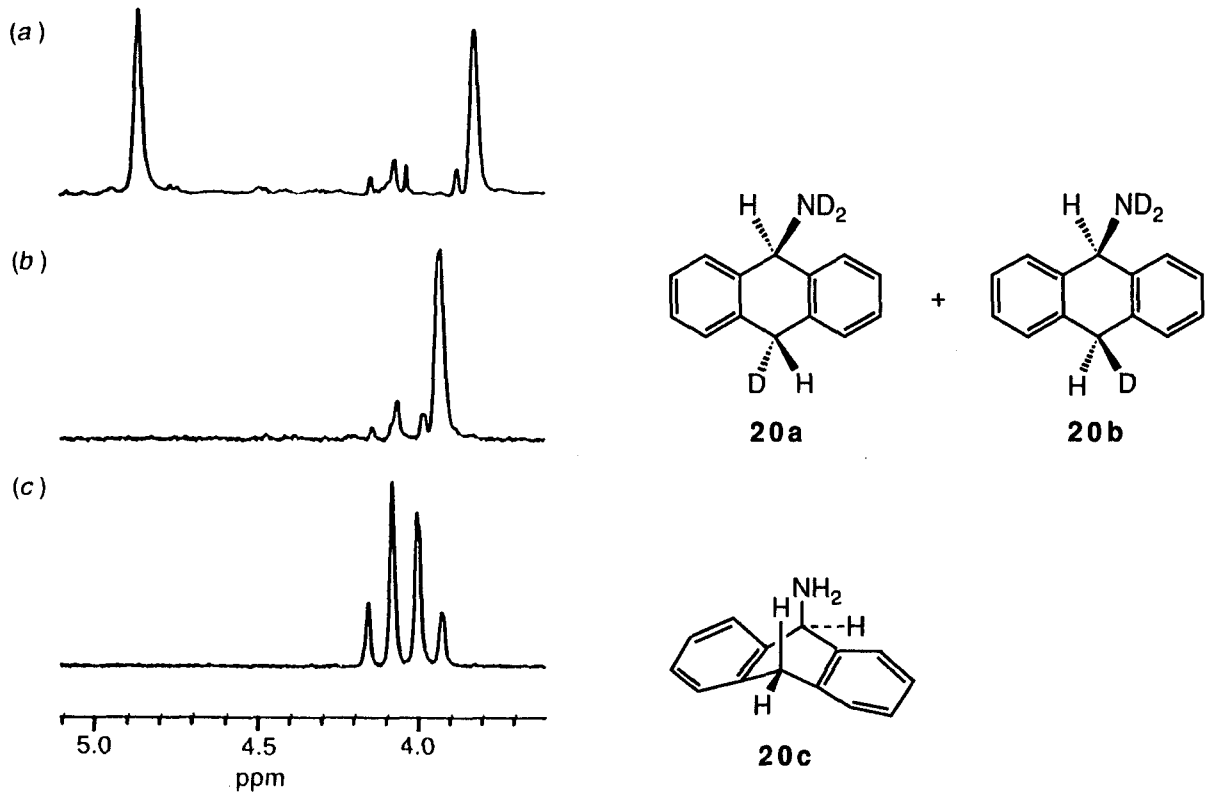


Fig. 6. ^{1}H NMR spectra of (a) **20a** and **20b**, and (b) the acetamides of **20b**, and (c) the acetamide of **20c** in the 3.6-5.1 ppm region

In the case of anthracene **1c**, 1,4-addition of ammonia occurred to give 9-amino-9,10-dihydroanthracene (**20c**). The axial conformer *ax*-**20c** in which the amino group occupies an axial position is suggested to be more stable than the equatorial one *eq*-**20c** from ^{1}H NMR studies[17] and molecular mechanics calculation,[18] as shown in Scheme 9. In the ^{1}H NMR spectrum [Fig. 6(c)] of the acetamide of **20c**, doublets at 3.96 ppm and 4.12 ppm can be assigned to be equatorial and axial proton of the methylene group, respectively, since the equatorial proton experiences the strong deshielding effect of the aromatic ring. The ^{1}H NMR spectra [Fig. 6(a) and 6(b)] for parent and the acetamide of 9-(*N*,*N*-dideuterioamino)-10-deuterio-9,10-dihydroanthracene (**20a,b**) formed from the photoamination of **1c** with ammonia-d_3 show that a deuterium atom was incorporated mainly at the equatorial position of the C-10 methylene group, demonstrating that 1,4-addition of ammonia to **1c** occurs in a predominantly *trans* manner (Scheme 10).

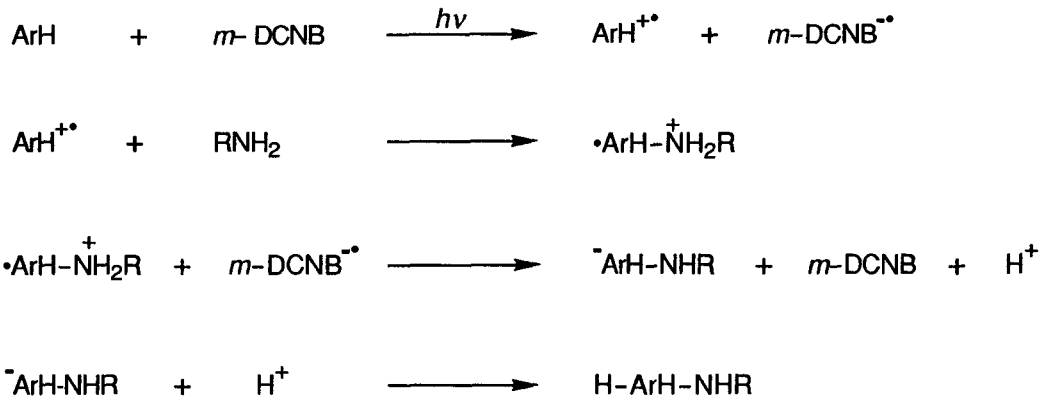
Mechanism. As has been discussed previously, for the photoamination of **1a** in Section 2-1, photoinduced electron transfer from **1a-c** and **11-12** to *m*-DCNB is responsible for the initiation process of the photoamination, since the fluorescence of these arenes (ArH) was quenched by *m*-DCNB at a diffusion-controlled limit, and the free energy change for electron transfer from the excited singlet state of ArH to *m*-DCNB was caluclated to be substantially negative by the Rehm-Weller equation,[19] as shown in Table 8. Therefore, the photoamination of **1a-c** and **11-12** proceeds via nucleophilic addition of ammonia or amine to the cation radicals[8]. The aminated cation radicals are deprotonated by amine and undergo reduction by an anion radical of *m*-DCNB followed by protonation (Scheme 11).

In the case of aminated products **13-16** from phenanthrene derivatives **1a-b**, **11-12**, the configuration around C-9 and C-10 can be related to the conformation of the aminated anions (**21**). The electron pair of **21** may exist in an axial position which is favourable for maximum orbital overlap of the electron pair with the aromatic ring. The resulting aminated anions **21** may adopt either configuration *ax*-**21** or *eq*-**21**, depending on the bulkiness of the amine as

Table 8. Rate Constants and Calculated Free Energy Changes for Fluorescence Quenching of arenes with *m*-DCNB

Arene	$E_{1/2}^{ox}$[a] / V	τ_f[b] / ns	$E_{0\text{-}0}$[c] / kJ mol^{-1}	K_{sv}[d] / dm^3 mol^{-1}	k_q[e] / 10^{10}dm^3 mol^{-1} s^{-1}	ΔG[f] / k mol^{-1}
1b	0.97	25	327	350	1.4	-35.1
11	0.93	25	329	240	0.96	-41.0
12	0.72	26	329	600	2.3	-61.1
1a	1.29	53	347	296	0.56	-24.3
1c	0.93	5.3	319	75	1.4	-31.4

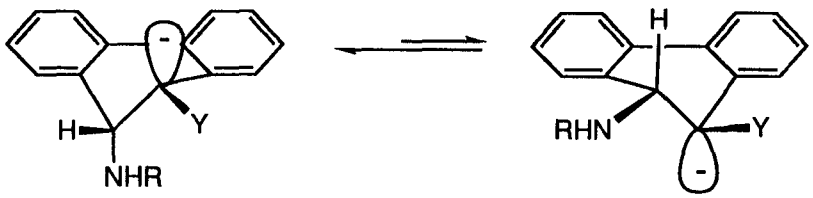
[a] Oxidation potentials in acetonitrile *vs.* Ag/AgNO$_3$. [b] Lifetime of fluorescence. [c] Excitation energy for the excited singlet of the arene estimated from fluorescence spectra. [d] Stern-Volmer constants for fluorescence quenching of arene. [e] Rate constants for fluorescence quenching of arene. [f] Calculated free energy change by Rehm-Weller equation (ref. 19).



Scheme 11.

shown in Scheme 12. Steric interactions between the amino group on C-9 and the substituent on C-10 may be expected to favor *ax*-**21**. It has been reported that the 9,10-dialkyl-9,10-dihydrophenanthryl anion adopts predominatly the cis arrangement between the two alkyl groups rather than trans.[20] Thus mainly cis isomers were formed on protonation of *ax*-**21**.

In the case of **1c**, trans 1,4-addition of ammonia occurs selectively. However, it is difficult to explain the trans addition of ammonia to **1c** in a similar way to the case of phenanthrene derivatives, since it is assumed, from a similar consideration to that applied in the case of the phenanthrene moiety, that both the amino group and the anion orbital occupy axial positions. Probably the amino group lies in the equatorial position because of the occurrence of the electrostatic repulsion between the anion and the lone pair of the amino group.



ax-**21** Y = H, OR *eq*-**21**

Scheme 12.

2-2-3 Experimental

^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ solutions using a Bruker AC-250P spectrometer. *J* value are in Hz. Mass spectra were recorded on a JEOL D-300S instrument.

Fluorescence spectra were measured on a Hitachi MPF-4 instrument. Fluorescence lifetimes were measured on a Horiba NAES 550 instrument by a single-photon-counting method. GLC analysis was performed on a Shimadzu GC-8A or GC-14A using OV-17 or capillray column. Oxidation potentials were measured in acetonitrile using a Hokuto Denko HA-501G and HB-105 as potentiostat and function generator.

Marerials. Commercially available **1a** was used after purification by column chromatography on a silica gel. 9-Alkoxyphenanthrene **1b**, **11** were prepared from 9-bromophenanthrene by the reported method.[21] According to the reported method,[22] **12** was prepared from the reaction of 9-phenanthrol with 1,2-bromoethane, followed by cyanation with NaCN and the subsequent reduction with $LiAlH_4$. Primary amines were purified by distillation from sodium metal. Ammonia-d_3 was prepared from the reaction of Mg_2N_3 with D_2O. Pheneathrene-d_{10} was prepared by treatment of phenanthrene with D_2O in the presence of BF_3.[23]

Photoamination of Arenes with Ammonia and Primary Amines. General Procedure. In 140 mL of 9:1 (V:V) acetonitrile-water solution was dissolved a mixture of an arene (14 mmol), an electron acceptor (3.5 mmol), and an amine (140-350 mmol), and then solution was purged with argon for 20 min. In the case of ammonia, ammonia gas was bubbled into argon-bubbled 9:1 (v:v) acetonitrile-water solutions containing arene and an electron acceptor. The solutions were irradiated with an Eikosha PIH-300 high-pressure mercury lamp through Pyrex under cooling with water. Details of the follow-up process have been described in the literature.[4,21]

12: ^{1}H NMR δ = 1.66 (2H, br s), 2.07-2.17 (2H, m), 3.05 (2H, t, J = 6.8 Hz), 4.33 (2H, t, J = 6 Hz), 6.99 (1H, s) 7.45-7.77 (5H, m), 8.36 (1H, dd, J = 8.0 and 1.9 Hz), 8.56-8.59 (1H, m), and 6.60 (1H, d, J = 7.8 Hz); ^{13}C NMR δ = 32.93, 39.44, 65.83, 102.61, 122.48, 122.53, 124.20, 126.36, 126.58, 127.11, 127.27, 131.23, 132.90, and 152.70; MS *m/z* 251 (M^+).

The photoamination of **1a** *and* **1c** *with ammonia-d_3.* The ^{1}H NMR spectrum of the aminated products (**18a-c**) obtained from the photoamination of **1a** with ammonia-d_3 shows that the integral ratio of signals at δ = 2.90, 3.12 and 4.08 ppm was 0.853 : 0.241 : 1,

revealing that **18a**, **18b** and **18c** were formed in a ratio of 75.9 : 14.7 : 9.5. Moreover, the ^{1}H NMR spectrum in the case of **5** shows that the integral ratio for signals of δ = 3.82, 4.15 and 4.86 ppm was 0.964 : 0.252 : 1, showing that **20a**, **20b** and **20c** were formed in a ratio of 74.8 : 3.6 : 21.6.

*cis-Amino-10-methoxy-9,10-dihydrophenanthrene (**13a**)*:[4, 21] ^{1}H NMR δ = 1.92 (2H, br s), 3.40 (3H, s), 4.14 (1H, d, J = 3.7 Hz), 4.26 (1H, d, J = 3.7 Hz), 7.28-7.48 (6H, m), and 7.73-7.78 (2H, m); ^{13}C NMR δ = 52.19, 56.86, 81.55, 123.77, 124.07, 127.17, 127.50, 1327.99, 128.15, 128.25, 128.75, 132.80, 133.05, 133.94, and 137.51.

*trans-Amino-10-methoxy-9,10-dihydrophenanthrene (**13b**)*: ^{1}H NMR δ = 1.92 (2H, br s), 3.38 (3H, s), 4.10 (1H, d, J = 5.4 Hz), 4.18 (1H, d, J = 5.4 Hz), 7.28-7.48 (6H, m), and 7.73-7.78 (2H, m); ^{13}C NMR δ = 54.13, 57.47, 83.27, 123.37, 124.28, 127.58, 127.84, 128.25, 128.43, 129.17, 129.54, 131.94, 133.05, 135.88, and 138.25.

*cis-9-Amino-10-ethoxy-9,10-dihydrophenanthrene (**14a**)*: ^{1}H NMR δ = 1.26 (3H, t, J = 6.9 Hz), 1.94 (2H, br s), 3.62 (2H, q, J = 6.9 Hz), 4.13 (1H, d, J = 3.7 Hz), 4.47 (1H, d, J = 3.7 Hz), 7.26-7.44 (4H, m), 7.49-7.76 (2H, m), and 7.75 (2H, d, J = 7.1 Hz); ^{13}C NMR δ = 15.40, 52.28, 64.77, 79.31, 123.81, 123.89, 127.49, 127.72, 127.97, 128.19, 128.25, 128.34, 1232.83, 132.94, 134.64, and 137.42. The acetamide; mp 169.5-170.5 °C; Found: C, 76.40; H, 6.55; N, 4.80 %. Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.98 %.

*trans-9-Amino-10-ethoxy-9,10-dihydrophenanthrene (**14b**)*: ^{1}H NMR δ = 1.24 (3H, t, J = 6.9 Hz), 1.94 (2H, br s), 3.73 (2H, q, J = 6.9 Hz), 4.07 (1H, d, J = 7.2 Hz), 4.27 (1H, d, J = 7.2 Hz), 7.26-7.44 (4H, m), 7.49-7.76 (2H, m), and 7.75 (2H, d, J = 7.1 Hz); ^{13}C NMR δ = 15.40, 54.44, 65.92, 81.92, 124.16, 124.52, 126.92, 127.94, 128.19, 128.71, 128.96, 129.43, 132.34, 133.31, 134.75, and 138.24.

*cis-9-(N-Isopropylamino)-10-methoxy-9,10-dihydrophenanthrene (**15a**)*: ^{1}H NMR δ = 1.01 (3H, d, J = 6.1 Hz), 1.17 (3H, d, J = 6.2 Hz), 1.71 (1H, br s), 3.01-3.05 (1H, m), 3.35 (3H, s), 4.03 (1H, d, J = 3.5 Hz), 4.35 (1H, d, J = 3.5 Hz), 7.20-7.46 (6H, m), and 7.73-7.85 (2H, m); ^{13}C NMR δ = 23.05, 23.57, 45.33, 55.58, 56.60, 78.35, 123.78, 124.08, 127.25, 127.41, 127.52, 127.82, 128.59, 128.88, 133.02, 134.1, and 137.41.

*cis-9-(tert-Butylamino)-10-ethoxy-9,10-dihydrophenanthrene (**16a**)*: ^{1}H NMR δ = 1.07 (3H, t, J = 6.9 Hz), 1.19 (9H, s), 1.81 (1H, br s), 3.42 (2H, q, J = 6.9 Hz), 4.03 (1H, d, J = 3.4 Hz), 4.29 (1H, d, J = 3.4 Hz), 7.22-7.44 (6H, m), 7.69-7.73 (1H, m), 7.80 (1H, d, J = 7.7 Hz), and 7.89-7.06 (1H, m); ^{13}C NMR δ = 15.10, 30.36, 50.88, 53.68, 63.72, 79.56, 123.31, 124.13, 126.89, 127.90, 128.04, 129.08, 133.13, 134.29, 134.64, and 139.67.

*cis-8b,10,11,12,13,13a-Hexahydrophenanthro[9.10-b]-4-oxazepine (**17a**)*: ^{1}H NMR δ = 1.86-2.04 (2H, m), 2.64 (1H, br s), 3.08 (2H, t, J = 5.4 Hz), 3.97 (2H, t, J = 5.5 Hz), 4.17 (1H, d, J = 4.2 Hz), 4.84 (1H, d, J = 4.2 Hz), and 7.14-7.78 (8H, m); ^{13}C NMR δ = 33.55, 45.58, 60.28, 66.47, 78.46, 123.45, 123.73, 127.57, 128.05, 128.05, 128.14, 128.20, 128.30, 132.48, 132.96, 133.75 and 138.00.

*trans-8b,10,11,12,13,13a-Hexahydrophenanthro[9.10-b]-4-oxazepine (**17b**)*: ^{1}H NMR δ = 1.86-2.04 (2H, m), 2.64 (1H, br s), 2.91-3.04 (2H, m), 3.91 (1H, d, J = 7.1 Hz), 4.21-4.31 (2H, m), 4.40 (1H, d, J = 7.1 Hz), and 7.14-7.77 (8H, m); ^{13}C NMR δ = 34.32, 44.90, 63.37, 69.06, 84.66, 123.47, 123.62, 127.45, 127.62, 127.84, 128.20, 128.30, 130.93, 132.69, 133.57, and 137.75.

*3-[N-(9-phenanthryl)amino]propanol (**17c**)*: ^{1}H NMR δ = 1.86-2.04 (2H, m), 2.64 (2H, br s), 3.41 (2H, t, J = 6.2 Hz), 3.77 (2H, t, J = 5.7 Hz), 6.73 (1H, s), 7.14-7.77 (5H, m), 7.86 (1H, d, J = 8.8 Hz), 8.49 (1H, d, J = 8.1 Hz), and 8.65 (1H, d, J = 7.8 Hz); ^{13}C NMR δ = 31.22, 42.60, 61.79, 101.61, 122.71, 123.32, 123.75, 124.24, 125.43, 126.20, 126.44, 126.47, 127.67, 127.90, 135.30, 135.59, and 141.44.

*X-Ray Crystal Diffraction Analysis of the Acetamide of **13a**.* The sample was recrystallized from methanol.

Crystal data. $C_{17}H_{17}O_2N$, M = 267.33, monoclinic, a = 13.085(5), b = 12.955(6), c = 9.125(5) Å, α = 90.07(4), β =1 09.48(4), γ= 89.95(3), V = 1457.4 Å^3, space group C_c, Z = 4, D_m = 1.22 Mg m^{-3}, D_x = 1.218 Mg m^{-3}, F(000) 568, λ = 0.710 69 A. Approximate crystal dimensions; 0.4×0.5×0.5 mm.

Data collection and processing. The intensity data were measured on a CAD-4 Enraf-Nonius diffractometer with graphite-monochromatized Mo-K_α radiation by ω-2θ scan technique. A total 4086 independent reflections were measured for $\theta < 30$, of which 737 were considered to be observed [$I > 3\sigma(I)$].

Structure analysis and refinement. The structure was solved by direct methods using MULTAN 82 and refined by full-matrix least-squares methods. In the final refinement anisotropic thermal parameters were used for non-hydrogen atoms. Hydrogen atoms were refined with isotropic thermal parameters. Final R and R_W values are 0.0895, 0.0897. There are no significant features in the final difference Fourier map. Anisotropic thermal parameters of non-hydrogen atoms and hydrogen atom-coordinates have been deposited at the Cambrige Crystallographic Data Centre (CCDC).

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Chapter 3

Elecron-Transfer Photosensitized Oxygenation of Stilbene and Naphthalene Derivatives in the Presence of Acetate Ion

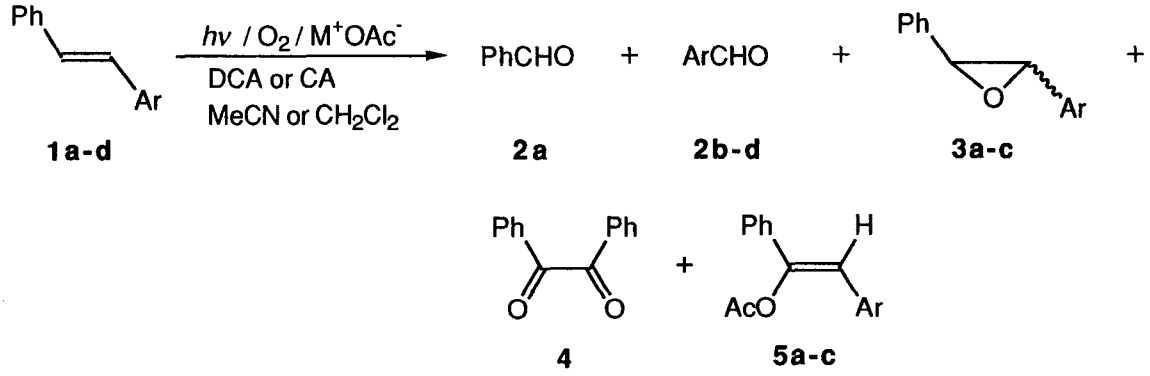
3-1 Introduction

A large amount of interest in photochemical electron transfer reactions has been directed toward controlling outcome of these processes.[1] The addition of salts is often effective to control photoreactions proceeding through exciplexs and ion radicals, since the charge separation and chemical reactivities of the ion radicals may be affected by interactions with salt ions as well as by a salt-induced increase in the solvent polarity.[2] Such salt effects can generally bring about remarkable changes in the reaction efficiencies, but usually produce no alteration of the reaction courses.[3,4] On the other hand, a nucleophile is well known to interact with cation radicals, resulting in the formation of a nucleophile-incorporated product in many cases. Therefore, nucleophiles have been used to trap cation species and for synthetic purposes. The author expected that a weak-nucleophilic salt may change the reaction courses of the cation radicals without the formation of any nucleophile-incorporated products. In Chapter 3, the author wishes to report on the photooxygenation of stilbene and naphthalene derivatives in the presence of weak-nucleophilic salts.

3-2 Results and Discussion

Photooxygenation of Stilbene Derivatives (1). To find effective weak-nucleophilic salts regarding photosensitized oxygenation, we performed a 9,10-dicyanoanthracene (DCA)-sensitized photooxygenation of *trans*-stilbene (**1a**) in the presence of $Et_4N^+X^-$ (X= OAc and OTs) or a complex of potassium salts (K^+X^-, X= OAc, OCN, $OCOCF_3$, and SCN) with 18-crown-6 ether. The photooxygenation was carried out by irradiating (> 400 nm) an O_2-saturated acetonitrile solution (40 mL) containing **1a** (2 mmol), DCA (0.02 mmol), and the salt

(4 mmol) by a high-pressure mercury lamp using an aqueous $CuSO_4/NH_3$ filter solution. The results are summarized in Table 1. The DCA-sensitized photooxygenation of **1a** in the presence of Et_4NOAc gave benzaldehyde **2a** (62%), *trans*-2,3-diphenyloxirane (**3a**, 7%), benzil (**4**, 1%), and 1-acethoxy-1,2-diphenylethene (**5a**, 9%) (run 1), as shown in Scheme 1. Table 1 shows that the addition of Et_4NOAc or KOAc/18-crown-6 ether was effective for the



a : Ar = Ph; **b** : Ar = 4-MeC_6H_4-; **c** : Ar = 4-$MeOC_6H_4$-; **d** : Ar= 3,5-$(MeO)_2C_6H_3$-

Scheme 1.

Table 1. DCA-Sensitized Photooxygenation of *trans*-Stilbene (**1a**) in the Presence of the Weak- or the Non-Nucleophilic Salts in MeCN[a]

Run No.	Salt[b]	Product Yield[c] / %				Recovery of **1a** / % (*Z*:*E*)[d]
		2a	**3a**	**4**	others	
1	Et_4NOAc	62	7	1	**5a** 9	31 (7:3)
2	Et_4NOTs	53	8	5		0
3	KOAc / 18-C-6	63	6	1	**5a** 9	11 (8:2)
4	KOCN / 18-C-6	43	1	1		22 (1:9)
5	$KOCOCF_3$ / 18-C-6	38	17	6		1 (6:4)
6	KSCN / 18-C-6	29	15	3		7 (4:6)
7	$Mg(ClO_4)_2$	34	18	0		0
8	Et_4NBF_4	34	11	1		0
9	none[e]	33	15	4		0

[a] For an O_2-saturated acetonitrile (40 mL) solution containing **1a** (2 mmol), DCA (0.02 mmol) and the salt (4 mmol). [b] 18-C-6; 18-crown-6 ether. [c] GLC yields based on consumed **1a**. [d] Isomer ratio of *cis*- to *trans*-**1a**. [e] In the absence of the salt.

formation of **2a**, since the DCA-sensitized photooxygenation of **1a** in the absence of the salt (run 9) gave **2a**, **3a**, and **4** in 33, 15, and 4% yields, respectively, as has been reported by Foote et al.[5] Although the addition of Et_4NOTs or KOCN/18-crown-6 ether was moderately effective, the addition of $KOCOCF_3$/18-crown-6 ether or KSCN/18-crown-6 ether was not effective. It was confirmed that the effect of Et_4NOAc was different from the usual effects of non-nucleophilic salts, such as $Mg(ClO_4)_2$ and Et_4NBF_4, since DCA-sensitized photooxygenation in the presence of $Mg(ClO_4)_2$ or Et_4NBF_4 (runs 7 and 8) gave a similar product distribution as that in the absence of the salt (run 9). Therefore, Et_4NOAc was used as a weak-nucleophilic salt throughout the present investigation.

The photooxygenations of substituted *trans*-stilbenes (**1b-d**) in the presence of Et_4NOAc in MeCN were carried out by using 9-cyanoanthracene (CA) as a sensitizer (Table 2), since the yield of **2a** was improved in CA-photosensitization, *i.e.* the CA-sensitized photooxygenation of **1a** gave exclusively **2a** in 79 % yield (run 10). The CA-sensitized photooxygenation of

Table 2. CA-Sensitized Photooxygenation of *trans*-Stilbene Derivatives (**1a-d**) in the Presence of Et_4NOAc[a]

Run No.	1	Solvent	Products (Yield[b] / %)				Recovery of 1 / % (Z:E)[c]	
10	**1a**	MeCN	**2a** (79)				20	(5:5)
11	**1a**[d]	MeCN	**2a** (37)		**3a**(13)	**4**(4)	29	(4:6)
12	**1b**	MeCN	**2a** (82)	**2b** (77)			0	
13	**1b**[d]	MeCN	**2a** (28)	**2b** (24)	**3b**(24)		7	(7:3)
14	**1c**	MeCN	**2a** (93)	**2c** (66)			0	
15	**1c**[d]	MeCN	**2a** (31)	**2c** (19)	**3c**(65)		38	(4:6)
16	**1d**	MeCN		-[e]			100	(6:4)
17[f]	**1d**	MeCN	**2a** (53)	**2d** (44)			61	(7:3)
18	**1b**	CH_2Cl_2	**2a** (32)	**2b** (23)		**5b**(44)	72	(3:7)
19	**1c**	CH_2Cl_2	**2a** (46)	**2c** (34)	**3c**(20)	**5c**(10)	5	(0:1)

[a] For an O_2-saturated MeCN or CH_2Cl_2 (40 mL) solution containing **1** (1 mmol), CA (0.02 mmol) and Et_4NOAc (4 mmol). [b] GLC yields based on consumed **1**. [c] Isomer ratio of *cis*- to *trans*-**1**. [d] In the absence of Et_4NOAc. [e] No reaction. [f] DCA-sensitized photooxygenation.

trans-4-methylstilbene (**1b**) and *trans*-4-methoxystilbene (**1c**) in the presence of Et_4NOAc (runs 12 and 14) gave 4-methylbenzaldehyde (**2b**) and 4-methoxybenzaldehyde (**2c**), respectively, as well as **2a**. The CA-sensitized photooxygenation of **1a**, **1b** and **1c** in the absence of Et_4NOAc gave the corresponding benzaldehydes (**2**) in low yields, accompanying the formation of **3a**, a mixture of *cis*- and *trans*-2-phenyl-3-(4-methylphenyl)oxirane (**3b**), and a mixture of *cis*- and *trans*-2-phenyl-3-(4-methoxyphenyl)oxirane (**3c**), respectively (runs 11, 13 and 15). Figure 1 shows the time-conversion curves for the CA-sensitized photooxygenation of **1b** in the presence of Et_4NOAc. Although the yields of **2a** and **2b** increased with an increase in conversion, **3b** was not formed, even at low conversion. It was found that the addition of Et_4NOAc entirely suppressed the formation of **3b.**

The CA-sensitized photooxygenation of **1b** and **1c** in CH_2Cl_2 gave considerable amounts of acetoxyl group-incorporated compounds, a mixture of *cis*- and *trans*-1-acetoxy-2-(4-methylphenyl)-1-phenylethene (**5b**) and a mixture of *cis*- and *trans*-1-acetoxy-2-(4-methoxyphenyl)-1-phenylethene (**5c**), as well as **2** and **3**, while **5b** and **5c** were not formed from the photooxygenation in MeCN. Moreover, although the CA-sensitized photooxygenation

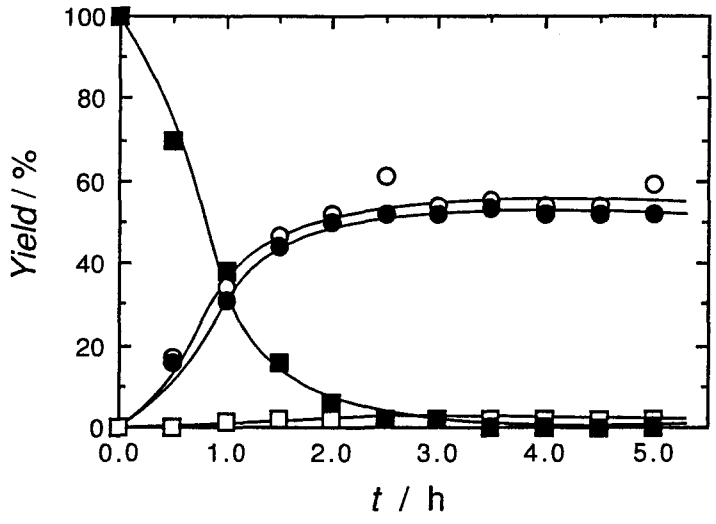
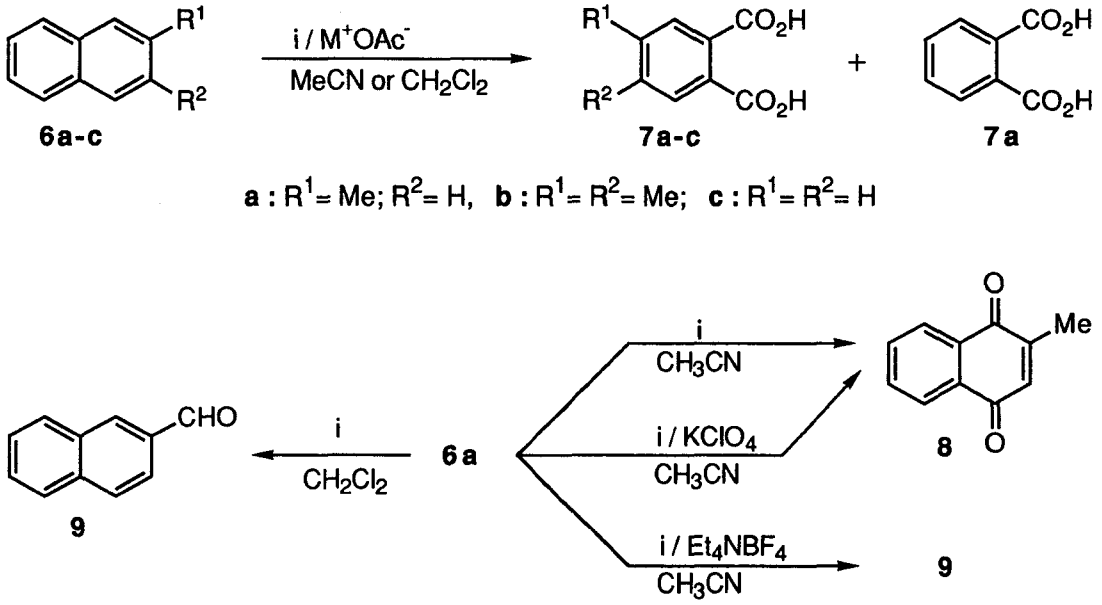


Fig. 1. Time-conversion curves for the disapperrance of **1b** (- ■ -) and for the formation of **2a** (- ○ -), **2b** (-● -), and **3b** (-□ -) for the CA-sensitized photooxygenation of **1b** in the presence of Et4NOAc.

of *trans*-3,5-dimethoxystilbene (**1d**) did not proceed in MeCN and CH_2Cl_2 at all, the DCA-sensitized photooxygenation of **1d** gave **2a** and **2d**.

Photooxygenation of Naphthalene Derivatives (6). Also, the effect of Et_4NOAc was investigated on the DCA-sensitized photooxygenation of **6**. The results are summarized in Table 3 and Scheme 2. The photooxygenation of 2-methylnaphthalene (**6a**) in the presence of Et_4NOAc or KOAc/18-crown-6 ether (runs 20 and 22) gave 4-methylphthalic acid (**7a**) and phthalic acid (**7c**), whereas the photooxygenation in the absence of Et_4NOAc gave only 2-methyl-1,4-naphthoquinone (**8**) (run 25). By contrast, Et_4NBF_4 and $KClO_4$ were not effective in the formation of **7** at all; the photooxygenation of **6a** gave **8** in the presence of $KClO_4$ (run 23) and 2-naphthaldehyde (**9**) in the presence of Et_4NBF_4 (run 24) at a low conversion of **6a** (<15%), though further irradiation resulted in the consumption of **8** and **9** without the accumulation of any other definite products. Similarly, the photooxygenation of 2,3-dimethylnaphthalene (**6b**) and naphthalene (**6c**) in the presence of Et_4NOAc gave the corresponding phthalic acids (**7**) (runs 26 and 27). Moreover, although the photooxygenation of **6a** in CH_2Cl_2 gave again **7a** and **7c** in the presence of Et_4NOAc (runs 28 and 30), it gave **9** in the absence of Et_4NOAc (runs 29 and 31).[6)]



Scheme 2. Reagents i: *hv* / O_2 / DCA

Table 3. DCA-Sensitized Photooxygenation of Naphthalene Derivatives (**6a-c**) in the Presence of the Salts[a]

Run No.	6	Salt[b]	Irradn. time / h	Products (Yield[c] / %)				Conversion of 6 / %
20	**6a**	Et4NOAc	7	**7a**	(21)	**7c**	(14)	74
21	**6a**	Et4NOAc	1	**7a**	(10)	**7c**	(7)	15
22	**6a**	KOAc / 18-C-6	6	**7a**	(27)	**7c**	(17)	63
23	**6a**	KClO4	0.5	**8**	(12)			11
24	**6a**	Et4NBF4	1	**9**	(37)			15
25	**6a**	none	0.3	**8**	(26)			7
26	**6b**	Et4NOAc	9	**7b**	(39)	**7c**	(22)	94
27	**6c**	Et4NOAc	7	**7c**	(50)			67
28[d,e]	**6a**	Et4NOAc	41	**7a**	(17)	**7c**	(12)	68
29[d,e]	**6a**	none	10	**9**	(24)			78
30[e]	**6a**	Et4NOAc	22	**7a**	(9)	**7c**	(9)	81
31[e]	**6a**	none	50	**9**	(44)			78

[a] For an O_2-saturated acetonitrile (40 mL) solution containing **6** (1 mmol), DCA (0.04 mmol) and the salt (4 mmol). [b] 18-C-6; 18-crown-6 ether, none; in the absence of the salt. [c] HPLC yields based on consumed **6**. [d] Irradiation without using an aqueous $CuSO_4$-NH_3 filter. [e] For a dichloromethane solution.

Quenching Experiment. Fluorescence quenching of DCA or CA by **1a-d** in MeCN and CH_2Cl_2 gave the Stern-Volmer constants (*Ksv*) and the quenching rate constants (*kq*) listed in Table 4. The fluorescence of DCA was efficiently quenched by Et4NOAc, while the fluorescence of CA was inefficiently quenched by Et4NOAc.

Mechanism. As has been reported for stilbene by Foote et al.[5] and for naphthalene derivatives by Santamaria,[7] an electron transfer from **1a** or **6a-c** to the excited singlet state of DCA or CA is responsible for the initiation process of the photooxygenation in the absence or presence of the salts. Also, the photooxygenation of **1b** and **1c** is certainly initiated by a photochemical electron transfer from **1b** or **1c** to CA, since the florescence of CA was efficiently quenched by **1b** and **1c**.

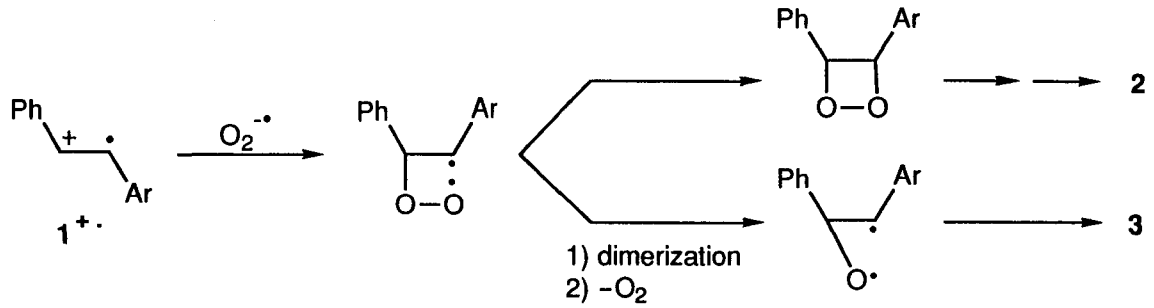
Table 4. Fluorescence Quenching of DCA and CA by Stilbene Derivatives (**1a-d**) and Et_4NOAc

Sensitizer	Solvent	Quencher	Ksv [a] / $dm^3\ mol^{-1}$	$kq \times 10^{10}$ [b] / $dm^3\ mol^{-1}\ s^{-1}$
DCA	MeCN	**1a**	248	1.6
	MeCN	**1d**	300	2.0
	MeCN	Et_4NOAc	192	1.3
CA	MeCN	**1a**	-	0.36[c]
	MeCN	**1b**	153	0.75
	MeCN	**1c**	210	1.0
	MeCN	**1d**	90	0.44
	MeCN	Et_4NOAc	<13	<0.06
	CH_2Cl_2	**1b**	86	0.9
	CH_2Cl_2	**1c**	193	2.0
	CH_2Cl_2	Et_4NOAc	8	0.09

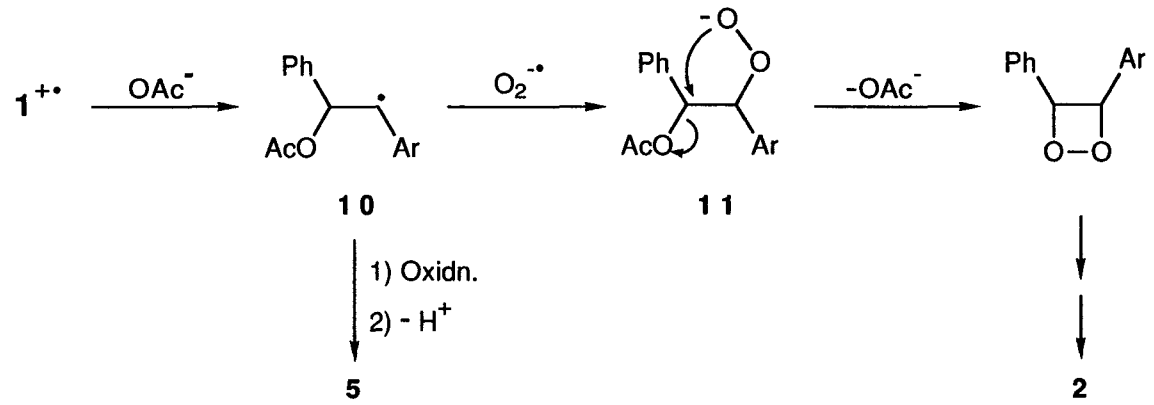
[a] Stern-Volmer constants for the fluorescence quenching. [b] Rate constants for the fluorescence quenching; $\tau_f = 15.3$ ns (DCA) in MeCN, $\tau_f = 20.5$ ns (CA) in MeCN, and $\tau_f = 9.4$ ns (CA) in CH_2Cl_2. [c] The value from Ref. 5a.

In the absence of the salt or in the presence of the non-nucleophilic salts, the resulting cation radicals of **1** react directly with $O_2^{-\bullet}$ generated by the oxidation of the anion radicals of CA or DCA to produce **2** and **3** (Scheme 3).[5] In the presence of M^+OAc^- (M= Et_4N and K/18-crown-6 ether), it is proposed that OAc^- reacts with $\mathbf{1}^{+\bullet}$ to give an adduct (**10**; •**1**-OAc) in competition with $O_2^{-\bullet}$, as shown in Scheme 4. The adduct, **10**, readily undergoes a radical coupling reaction with $O_2^{-\bullet}$ to give an intermediate (**11**; $^-$OO-**1**-OAc). Elimination of the acetoxyl group from **11** gives a dioxetane, since an acetoxyl group is a good leaving group. The dioxetane is well known to be a precursor for the formation of **2**.[8] Therefore, the formation of **11** is a key pathway for the formation of **2** in the presence of M^+OAc^-. Farid et al. have reported that both a nucleophile- and oxygen-incorporated intermediate was formed as an intermediate for the photooxygenation of 1,1-dimethylindene.[9] The formation of an adduct (•**1**-OAc) inhibits any direct reaction of $\mathbf{1}^{+\bullet}$ with $O_2^{-\bullet}$, resulting in the lack of **3**. It has been

confirmed that no formation of **2** occurred from the degradation of **3** by the reaction with OAc^- or O_2, since the DCA-sensitized photooxygenation of **3** in the presence of M^+OAc^- did not give **2**. Photooxygenation in the presence of the other weak nucleophiles, such as Et_4NOTs and KOCN/18-crown-6 ether, proceeds, to some extent, in a similar way as in the case of M^+OAc^-.



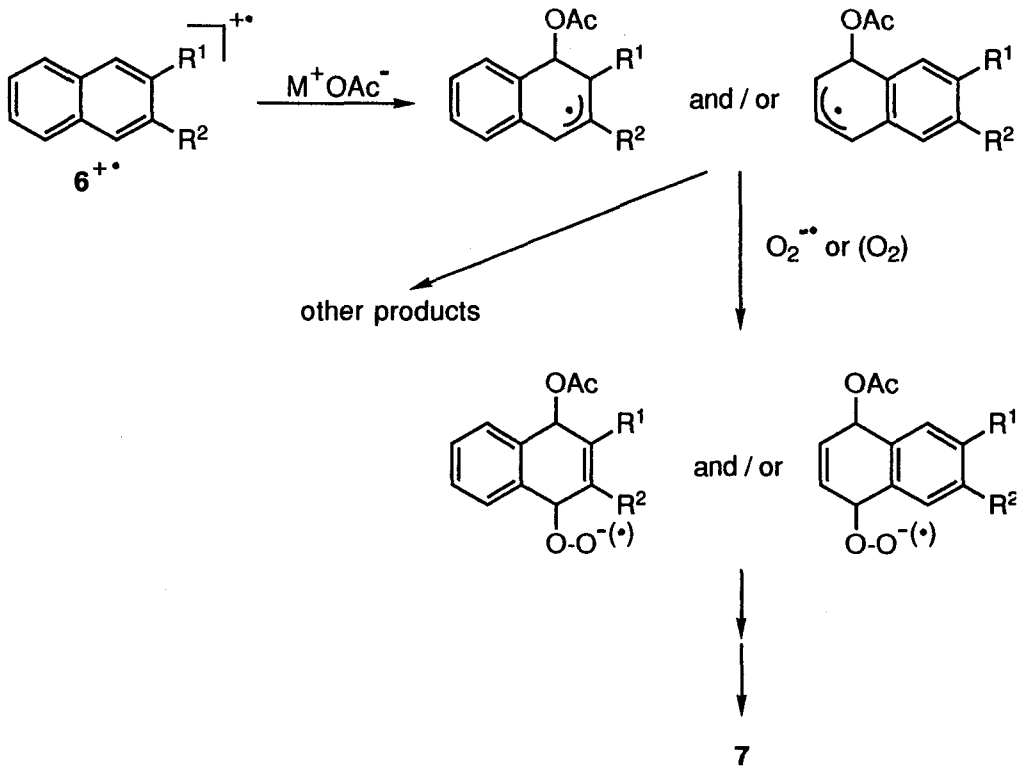
Scheme 3.



Scheme 4.

The formation of **10** was strongly supported by the formation of the acetoxyl group-incorporated product (**5**) during photooxygenation in the presence of M^+OAc^-. The formation of **5** proceeds by the nucleophilic addition of OAc^- to $\mathbf{1}^{+\bullet}$, followed by the oxidation with O_2 and subsequent deprotonation. Moreover, the acetoxylation of **1c** occurred selectively at the benzylic position of the phenyl group. This result is in accord with the selectivity of the photoamination of **1c** with ammonia, which proceeds by the nucleophilic addition of ammonia to the benzylic position of the phenyl group of $\mathbf{1c}^{+\bullet}$.[10]

Moreover, the photooxygenation of naphthalene derivatives (**6**) in the presence of M^+OAc^- occurs through a similar mechanism to the case of **1**; the reaction of the adduct radical (•**6**-OAc) with O_2 and/or related oxygen species gave **7a-c** as the final products, though mechanistic details for the follow-up processes are still unknown (Scheme 5). The specific oxygenation of the aromatic rings can be explained by this mechanism. Two kinds of phthalic acids were produced by the addition of OAc^- to both the substituted and unsubstituted ring of **6a** or **6b**.[11] In accord with this mechanism, lack of the formation of **7** in the presence of Et_4NBF_4 or $KClO_4$ can be easily explained in terms of the negligible or very weak nucleophilicity of BF_4^- and ClO_4^-. It is of synthetic significance to note that the selective oxidative cleavage of the aromatic rings by the DCA-sensitized photooxygenation of **6** in the presence of M^+OAc^- is in sharp contrast to the usual photooxygenations of alkylated arenes that generally result in the oxidation of alkyl substituents.[12]



Scheme 5.

These mechanistic speculations have been born out of our previous studies concerning the efficient addition of such nucleophiles as CN^-,[13] BH_4^-,[14] and RNH_2[15] to photogenerated cation radicals of aromatic hydrocarbons and stilbenes. The effect of non-nucleophilic salts, such as $Mg(ClO_4)_2$, on the photooxygenation via electron transfer has been understood by the stabilization of ion radicals by Coulombic interaction, resulting in the suppression of a back electron transfer between ion radicals.[3] The weak-nucleophlic salts bring about the unusual effects that are caused by nucleophilic additions to the cation radical, as well as complexation with the ion radicals. Thus, the present investigation reveals that the reaction courses of photooxygenation via electron transfer can be controlled by the use of non or weak-nuleophilic salts, as well as by the choice of solvents.

3-3 Experimental

^1H and ^{13}C NMR spectra were taken on a Bruker AC-250P spectrometer for $CDCl_3$ solutions with tetramethylsilane used as an internal standard. IR spectra were taken on a JASCO A-302 spectrometer. The fluorescence spectra were taken on a Hitachi MPF-4. The fluorescence lifetimes of DCA and CA were measured on a Horiba NAES 550 by a single-photon counting method. GLC and HPLC analyses were carried out on a Shimadzu GC-14A using a capillary column (CBP1-M25-025) and a JASCO HPLC system (875-UV, 860-CO, 880-PU, and an injector 7125), respectively.

Materials. Substituted stilbenes (**1b-d**) were prepared by the Wittig reaction of benzylphosphonium chloride with substituted benzaldehydes.[10] Commercially available **1a**, **6a-c**, DCA, and CA were purified by recrystallization. All salts and 18-crown-6 ether were purchased and used without further purification. Acetonitrile was distilled from P_2O_5, and then from CaH_2.

Photooxygenation of Stilbenes (1). Into a Pyrex vessel was introduced an acetonitrile solution (40 mL) containing **1** (2 mmol), sensitizer (0.02 mmol), and the salt (4 mmol), and then was bubbled with oxygen. The solution was irradiated with an Eikosha PIH-300 high-pressure mercury lamp through an aqueous $CuSO_4/NH_3$ filter solution. The analyses of **2**, **3**,

4, and **5** were performed by GLC. The identifications of **2a-d**, **3a-c** and **4** were performed by a direct comparison with an authentic sample in GLC analysis and NMR spectra. The authentic samples of **3a-c** were prepared by the reported methods.[16)]

*trans-2,3-Diphenyloxirane (**3a**)*: ^{1}H NMR δ = 3.86 (2H, s) and 7.29-7.46 (10H, m); ^{13}C NMR δ = 62.82, 125.47, 128.30, 128.54, and 137.67.

*trans-2-Phenyl-3-(4-methylphenyl)oxirane (**3b**)*: ^{1}H NMR δ = 2.37 (3H, s), 3.85 (2H, d, J = 4.2 Hz), 7.12-7.25 (4H, m), and 7.32-7.41 (5H, m); ^{13}C NMR δ = 21.24, 62.78, 62.89, 125.45, 128.25, 128.54, 129.25, 134.07, 137.20, and 137.18.

*trans-2-Phenyl-3-(4-methoxylphenyl)oxirane (**3c**)*: ^{1}H NMR δ = 3.67 (3H, s), 4.99 (1H, d, J = 7.5 Hz), 6.04 (1H, d, J= 7.5 Hz), and 7.06-7.33 (9H, m); ^{13}C NMR δ = 55.08, 76.60, 80.63, 113.67, 127.15, 128.10, 128.63, 129.64, 130.01, 134.44, and 139.16.

*1-Acetoxy-1,2-diphenylethene (**5a**)*: ^{1}H NMR δ = 2.21 (3H, s), 6.86 (3H, s), 7.37-7.52 (8H, m), and 7.94 (2H, d, J = 8.3 Hz); ^{13}C NMR δ = 20.81, 128.65, 128.72, 128.81, 128.71, 129.17, 129.37, 130.00, 130.31, 133.53, 133.53, 134.49, and 170.52.

*One isomer of 1-acetoxy-2-(4-methylphenyl)-1-phenylethene (**5b**)*: ^{13}C NMR δ = 20.83, 21.68, 128.60, 128.68, 128.92, 129.10, 129.29, 129.33, 131.91, 133.43, 133.79, 134.50, and 170.50.

*One isomer of 1-acetoxy-2-(4-methoxyphenyl)-1-phenylethene (**5c**)*: ^{13}C NMR δ = 20.85, 55.45, 113.86, 128.47, 128.64, 129.11, 129.25, 130.16, 131.19, 132.10, 134.01, 163.74, and 170.57.

The adduct (**5c**) from the photooxygenation of **1c** was isolated as a mixture of *trans* and *cis* isomer, but it was confirmed that the adduct was not 1-acetoxy-1-(4-methoxyphenyl)-2-phenylethene (**5c'**), which was prepared from the reaction of **1c** (5 mmol) with acetic acid (60 mL) in the presence of $Pd(OAc)_2$ (5 mmol), $Cu(OAc)_2$ (5 mmol), and LiCl (5 mmol) at 70 °C[17)].

*One isomer of **5c'***: ^{13}C NMR δ = 20.99, 55.13, 113.57, 127.56, 127.56, 128.04, 128.19, 128.32, 128.85, 129.35, 129.93, 159.45, and 169.89.

Photooxygenation of Naphthalene Derivatives (6). An O_2-saturated acetonitrile solution (40 mL) containing **6**, DCA (0.04 mmol), and the salt (4 mmol) was irradiated in a similar way as in the case of **1**. Product analyses were carried out on HPLC. The identification of **7a**, **7c**, **8**, and **9** was performed by direct comparisons with commercially available authentic samples. *Dimethyl ester of 7b*: ^{1}H NMR δ = 2.30 (3H, s), 3.85 (6H, s), and 7.41 (2H, s); IR ($CHCl_3$) 1720 cm^{-1} (CO).

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Chapter 4

Synthetic Application of Photoinduced Electron-Transfer Reaction

4-1 Phosphonation of Arenes with Trialkyl Phosphites

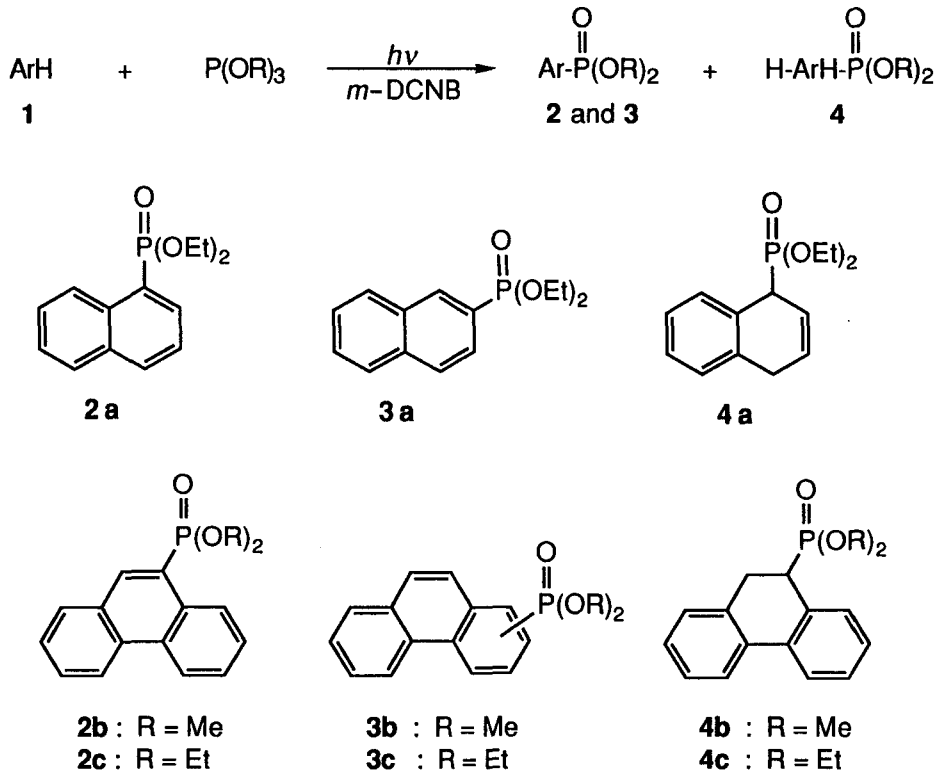
4-1-2 Introduction

The formation of carbon-phosphorus bonds has synthetic potential. The synthesis of arylphosphonates is achieved by the reaction of aryl halide with dialkyl phosphonates or trialkyl phosphites in the presence of metal catalyst,[1] and the photoreaction of aryl halide with dialkyl phosphite anions[2] or trialkyl phosphites[3] as well as the Friedel-Crafts reaction of arenes with phosphours trichloride followed by alcoholysis,[4] since usual Arbuzov reaction is not applicable to the formation of aryl carbon-phosphours bonds. However, only few methods have been reported for a direct introduction of the phosphonate group to aromatic hydrocarbons.[5]

As parts of investigation on synthetic application of photoinduced electron transfer, the author has extensively investigated the addition of nucleophiles to the cation radicals of aromatic hydrocarbons (ArH) generated by photoinduced electron transfer to electron acceptors.[6-8] Thus photochemical electron transfer has proved to be a useful tool for the direct introduction of functional groups, such as cyano and amino groups, to aromatic nuclei.[6,7] From these points of view, the author has investigated the direct photophosphonation of naphthalene and phenanthrene with trialkyl phosphites ($P(OR)_3$) in the presence of *m*-dicyanobenzene (*m*-DCNB) (Scheme 1.)

4-1-2 Results and Discussion

Irradiation of an acetonitrile solution containing naphthalene (**1a**), *m*-DCNB, and $P(OEt)_3$ under a nitrogen atmosphere by high-pressure mercury lamp gave diethyl 1-naphthylphoshonate (**2a**), diethyl 2-naphthylphoshonate (**3a**), and diethyl(1,4-dihydro-1-naphthyl)phosphonate (**4a**) in 39, 32, and 2% yields, respectively. In the case of phenanthrene (**1b**), diethyl 9-phenanthrylphoshonate (**2b**), the isomer of **2b** (**3b**), and diethyl (9,10-dihydro-9-phenanthryl)phosphonate (**4b**) were obtained in 33, 9, and 13% yields, respectively. The results are shown in Table 1. The arylphosphonates (**2** and **3**) was predominantly formed from a photoreaction in acetonitrile or *N*,*N*-dimethylformamide (DMF) under oxygen or nitrogen atomsphere, while more dihydroarylphoshonates (**4a** and **4b**) were formed in acetonitrile-water (19:1) than in acetonitrile. Moreover, *m*-DCNB was substantially consumed to give 1-alkyl-2,4-dicyanobenzenes (**5**) during the photophosphonation of **1b** with $P(OR)_3$ in acetonitrile, whereas high-yield *m*-DCNB was recoverd in the case of **1a**, as is shown in Table 2.



Scheme 1.

Table 1. Photophosphonation of Arenes with $P(OR)_3$[a]

1	R	Solvent / Atomsphere	Product (Yield[b] / %)			Conv. of 1/%	Recov.of *m*-DCNB/%
1a	Et	CH_3CN / N_2	**2a** (39)	**3a** (32)	**4a** (2)	85	64
1a	Et	CH_3CN-H_2O (19:1) / N_2	**2a** (18)	**3a** (32)	**4a** (13)	65	72
1b	Et	CH_3CN / N_2	**2b** (33)	**3b** (9)	**4b** (13)	74	32
1b	Et	CH_3CN-H_2O (19:1) / N_2	**2b** (12)	**3b** (14)	**4b** (52)	84	76
1b	Me	CH_3CN / O_2	**2c** (58)	**3c** (17)	**4c** (20)	96	78
1b	Me	DMF / O_2	**2c** (52)	**3c** (7)	**4c** (4)	88	80

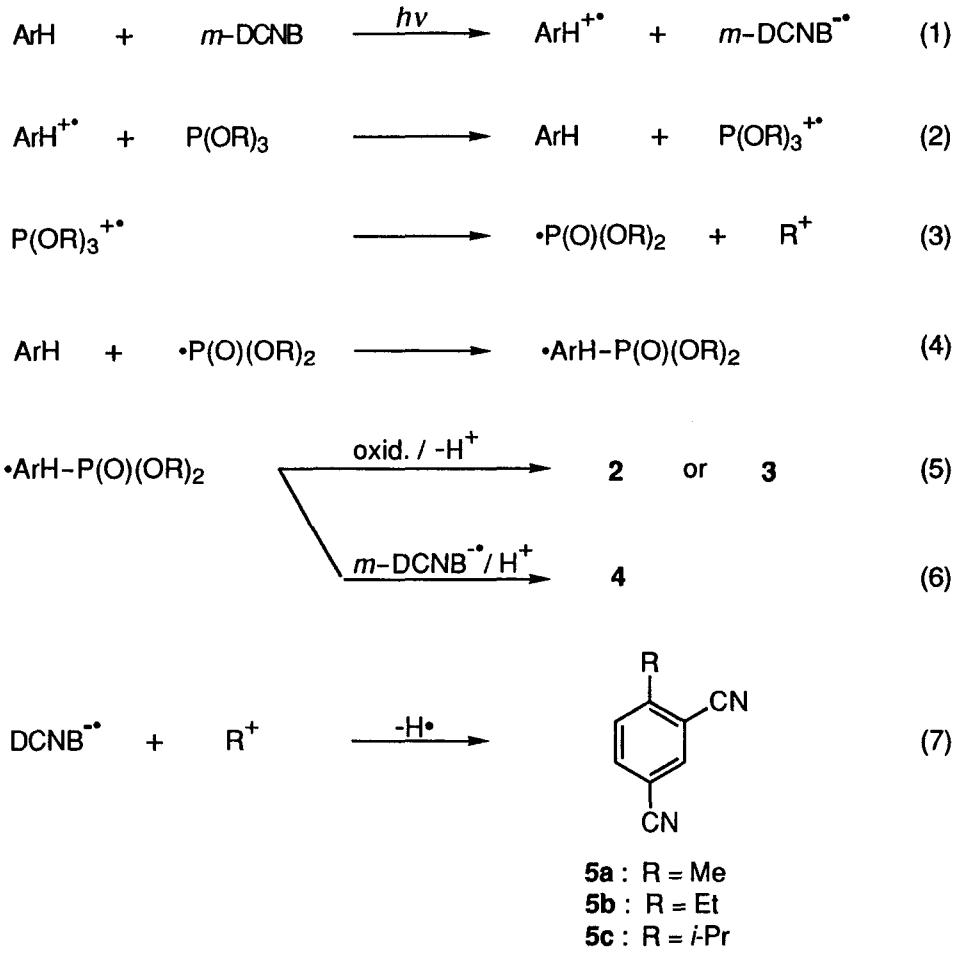
[a] See text. [b] Isolated yields based on arene used.

Table 2. The Formation of 1-Alkyl-2,4-dicyanobenzene (**5**) from the Photoreaction of **1b** with $P(OR)_3$ in the Presence of *m*-DCNB[a]

R	Irradn. time / h	Products (Yield[b] / %)	Conv. of *m*-DCNB / %	Recov.of **1b** / %
Me	70	**5a** (15)	15	43
Et	58	**5b** (62)	80	50
Et	60[c]	**5b** (0)	8	-
i-Pr	55	**5c** (32)	82	13

[a] For 100 mL of acetonitrile solution containing *m*-DCNB (5 mmol), $P(OR)_3$ (50 mmol), and **1b** (5 mmol). [b] Isolated yields based on *m*-DCNB used. [c] In the absence of **1b**.

The photophosphonation was initiated by electron transfer from the excited singlet state of ArH to *m*-DCNB to generate the cation radical of ArH ($ArH^{+\bullet}$) and the anion radical of *m*-DCNB (*m*-$DCNB^{-\bullet}$) (Eq. 1), since the photoreactions were carried out under conditions in which the fluorescene of **1a** or **1b** was exclusively quenched by *m*-DCNB, but negligibly by $P(OR)_3$. Notable observations of mechanistic significance are i) less regioselectivity compared with photoamination by amines and photocyanation by cyanide anion, [6,7] ii) the close oxidation potentials of $P(OR)_3$ to that of ArH, *i.e.* $E^{ox}_{1/2}$ ($P(OEt)_3$) = 1.25, $E^{ox}_{1/2}$ (**1a**) = 1.22,[8] and $E^{ox}_{1/2}$ (**1b**) = 1.17,[8] and iii) a considerable consumption of *m*-DCNB.



It has ben reported that the nucleophiles, such as cyanide anion and amines, added selectively at C-1 of $\mathbf{1a}^{+\bullet}$ or at C-9 of $\mathbf{1b}^{+\bullet}$, where the highest positive charge might develop.[6a,7] However, photophosphonation is too less-chemoselective to proceed only by a nucleophilic addition of $P(OR)_3$ to $ArH^{+\bullet}$. Previous studies on photoamination showed that the dialkylamines with the oxidation potentials close to that of ArH undergo an electron exchange with $ArH^{+\bullet}$ in competition with nucleophilic addition.[6b] From the above observations, it is, therefore, strongly suggested that the electron exchange between $P(OR)_3$ and $ArH^{+\bullet}$ occurs to generate $P(OR)_3^{+\bullet}$ which would decompose to the dialkoxyphosphoryl radicals and carbocation (Eqs. 2 and 3). The less regioselective phosphonation can be attributed to the addition of the $\bullet P(O)(OR)_2$ to ArH, as is shown in Eqs 4-6. The resulting phosphorylaryl radicals become fully aromatic (**2** and **3**) upon oxidation followed by deprotonation to give and/or are reduced with *m*-$DCNB^{-\bullet}$ followed by protonation to give **4**. A

similar mechanism has been reported for the free-radical phosphonation by $\cdot P(O)(OR)_2$, generated from diethyl phosphonate and *t*-butyl peroxide.[5] Moreover, the formation of **5** would arise from the reaction of *m*-DCNB$^{-\bullet}$ with carbocation generated from $P(OR)_3^{+\bullet}$ (Eq. 7).

4-1-3 Experimental

The ^1H and ^{13}C NMR spectra were taken on a JEOL JNM 60 and a JEOL FX 90 spectrometer, respectively, for a $CDCl_3$ solutions using tetramethylsilane as an internal standard. Gas chromatography was performed on a Shimadzu GC-8A using a 50 cm column of 2% OV-17 on Chromosorb W. The fluorescence quenching experiments were performed for a degassed acetonitrile solution on a Hitachi MPF-4 spectrometer. Mass spectra were measured on a JEOL D-300S equipped with a JMA 2000 data analyzer. Measurements of oxidation potentials were performed for deaerated acetonitrile solutions containing $P(OEt)_3$ (1×10^{-3} mol dm^{-3}) and a supporting electrolyte, tetraethyl ammonium tetrafluoroborate (0.1 mol dm^{-3}), vs. $Ag/AgNO_3$ of reference electrode at 23 $\pm$ 0.1°C by a Hokuto Denko HA-501G potentiostat and a Hokuto Denko HB-105 voltage generator.

Photoreaction of Arenes. Irradiation was performed for a solution (100 mL) containing an arene (10 mmol), *m*-DCNB (5 mmol), and a trialkyl phosphite (50 mmol) by a high-pressure Hg lamp under cooling with water. After evaporation under reduced pressure, the photolysates were dissolved in 100 mL of benzene and then extracted with 50 mL of water. The benzene solution was chromatographed on silica gel with hexane, benzene, and ethyl acetate as a eluent; the products were thus isolated. The structure of **2a** or **2b** was determined by comparisons with authentic samples prepared from the reaction of 1-bromonaphthalene or 9-bromonaphthalene with sodium diethyl phosphite in the presence of cuppor (I) iodide. Although the structures of **3b** and **3c** could not unambiguously be determined, they were reduced to be 1-phenanthrylphosphonates from the ^1H NMR spectra. **4a-c** could not be purified due to rapid aromatization to **1a** or **1b** during purification.

Diethyl 1-Naphthylphosphonate (2a): ^{1}H NMR δ = 1.31 (6H, t, J = 7 Hz), 4.14 (4H, dq, J = 7 and 12 Hz), 7.46-7.69 (3H, m), and 7.86-8.58 (4H, m); ^{13}C NMR δ =16.3 (d, J = 6 Hz), 62.2 (d, J = 6 Hz), 124.2, 124.8, 126.3, 126.7 (d, J = 3 Hz), 127.4, 128.7, 128.8, 133.6, (d, J = 3 Hz), 133.9, and 134.6 (d, J = 9 Hz); MS *m/z* 264 (M^+), 235, 190, 155, and 138.

Diethyl 2-Naphthylphosphonate (3a): ^{1}H NMR δ = 1.35 (6H, t, J = 7Hz), 4.15 (4H, dq, J = 7 and 11 Hz), 7.5-8.0 (6H, m), and 8.42 (1H, d, J = 15 Hz); ^{13}C NMR δ =16.4 (d, J = 6 Hz), 62.2 (d, J = 5 Hz), 126.5 (d, J = 11 Hz), 126.9, 127.8, 128.0, 128.2, 128.8 (d, J = 7 Hz), 129.0, 132.1, 132.8, and 134.1 (d, J = 10 Hz); MS *m/z* 264; IR 1230 cm^{-1}.

Diethyl (1,4-Dihydro-1-naphthyl)phosphonate (4a): ^{1}H NMR δ = 1.2 and 1.3 (6H, t, J = 7 Hz), 3.4 (2H, m), 3.8 (4H, dq, J = 7 and 12 Hz), 4.1 (1H, m), 5.9-6.0 (2H, m), 7.0-7.1 (3H, m), and 7.2-7.25 (1H, m); MS *m/z* 266 (M^+) and 128; IR 1230 cm^{-1}.

Diethyl 9-Phenanthrylphosphonate (2b): ^{1}H NMR δ = 1.3 (6H, t, J = 7 Hz), 4.0 (4H, dq, J = 7 and 11 Hz), 7.6-7.7 (4H, m), 8.0 (1H, d, J = 8.1 Hz), and 8.5-8.7 (4H, m); ^{13}C NMR δ =16.4 (d, J = 6 Hz), 62.3 (d, J = 5 Hz), 122.6, 123.0 (d, J = 1 Hz), 127.0, 127.2, 127.2, 127.6 (d, J = 3 Hz), 129.2, 129.8 (d, J = 4 Hz), 130.0, 130.0, 130.5, 130.7, 132.3 (d, J = 3 Hz), and 138.2 (d, J = 9 Hz); MS *m/z* 314 (M^+), 205, and 178; IR 1250 cm^{-1}.

Isomer of 2b (3b): ^{1}H NMR δ = 1.3 (6H, t J = 7 Hz), 4.0 (4H, dq, J = 7 Hz), 7.3-7.8 (7H, m), 8.5-8.7 (1H, m), and 9.0 (1H, d, J = 16 Hz); ^{13}C NMR δ =16.3 (d, J = 6 Hz), 62.1 (d, J = 5 Hz), 122.5, 122.9, 126.2, 127.1, 127.8 (d, J = 7 Hz), 128.0 (d, J = 5 Hz), 128.4 (d, J = 3 Hz), 128.6, 128.9, 129.4, 130.0, 131.5, 132.1 (d, J = 3 Hz), and 134.3 (d, J = 9 Hz); MS *m/z* 314 (M^+), 286, 258, 240, 205, and 178; IR 1230 cm^{-1}.

Diethyl(9,10-Dihydro-9-phenanthryl)phosphonate (4b): ^{1}H NMR δ = 1.2-1.3 (6H, t, J = 7 Hz), 2.8-3.2 (2H, m), 3.3-3.4 (1H, m), 3.8 (4H, dt, J = 7 and 9 Hz), 7.0-7.2 (6H, m), and 7.46-7.7 (2H, m); MS *m/z* 316 (M^+), 206, and 178; IR 1250 cm^{-1}.

Dimethyl 9-Phenanthrylphosphonate (2c): ^{1}H NMR δ = 3.82 (6H, d, J = 11.5 Hz), 7.6-7.8 (4H, m), 7.9-8.1 (1H, m), and 8.4-8.8 (m, 4H); MS *m/z* 286 (M^+), 191, and 178.

Isomer of 2c (3c): ^{1}H NMR δ = 3.69 (6H, d, J = 11 Hz), 7.54-7.67 (3H, m), 7.74-7.86 (4H, m), 8.77 (1H, d, J = 8.2 Hz), and 9.13 (1H, d, J = 14 Hz); MS *m/z* 286 (M^+), 191, and 178; IR 1250 cm^{-1}.

Dimethyl(9,10-Dihydro-9-phenanthryl)phosphonate (4c): ^{1}H NMR δ = 3.0-3.95 (2H, m), 3.03 and 3.36 (6H, d, J = 10 Hz), 3.4-3.6 (4H, m), 7.03-7.23 (6H, m), and 7.47-7.67 (2H, m); MS *m/z* 288 (M^+) and 178; IR 1250 cm^{-1}.

The spectral data of 1-methyl and 1-ethyl-2,4-dicyanobenzenes (**5a-b**) have been reported;[6a] **5b**, mp 66-67 °C

1-Isopropyl-2,4-dicyanobenzene (5c): Mp 78-79 °C; ^{1}H NMR δ = 1.30 (6H, d, J = 6 Hz), 3.30 (1H, sept, J = 6 Hz), 7.13 (1H, d, J = 8 Hz), and 7.43 (1H, d, J = 8 Hz), and 7.50 (1H, s); MS *m/z* 170; IR 2240 cm^{-1}.

4-2 Synthesis of 1-Amino-2-tetralone by Photoamination of 2-Alkoxynaphthalenes with Alkylamines

4-2-1 Introduction

Nucleophlic additions induced by photochemical electron transfer have been extensively investigated and have become a useful tool to introduce certain functional groups to aromatic nuclei and olefins.[9] We have investigated the photoinduced nucleophilic addition of ammonia and amines to arenes, stilbenes, 1,1-diarylalkenes, and 1-aryl-propenes in previous Sections. It was found that the photoamination of naphthalene derivatives gave readily 1-amino-1,4-dihydro-naphthalenes of which synthesis by other methods has not been reported previously. Especially, the photoamination of 2-methoxynaphthalene occurred most efficiently and most selectively among naphthalene derivatives investigated. Therefore, our attention are paid to the preparation of a variety of 1-amino-1,4-dihydronaphthalenes by photoamination of 2-alkoxynaphthalenes and their synthetic application.

In this Section, the auther wishes to report the photoamination of several 2-alkoxynapthalenes with ammonia and alkylamines and of their application to synthesis of 1-amino-2-tetralones.

4-2-1 Results and Discussion

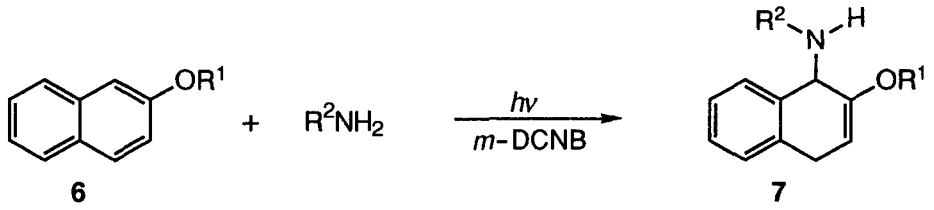
Photoamination. The photoaminations of 2-alkoxynaphthalenes **6** were carried out by irradiating a deaerated acetonitrile-water (9:1) solution containing the arene, *m*-dicyanobenzene (*m*-DCNB), and an amine by high-pressure mercury lamp through a Pyrex filter. The photoamination of 2-methoxynaphthalene **6a**, 2-ethoxynaphthalene **6b**, 2-isobutoxynaphthalene **6c**, and 2-benzyloxynaphthalene **6d** with ammonia and alkylamines gave the corresponding 1-alkylamino-2-alkoxy-1,4-dihydronaphthalene (AADN; **7**) as exclusive product (Scheme 2). The AADN was slowly decomposed into intractable materials by long-time exposure under oxygen atmosphere and was dehydroaminated into parent 2-alkoxynaphthalene when passed through a gas chromatograph over about 200 °C of injection temperature. But

Table 3. The Photoamination of 2-Alkoxynaphthalenes (**6**)[a]

ArH ($E_{1/2}^{ox}$ / V)[b]	R^2NH_2	Irradn time / h	Yield[c] / %		Recov. of ArH / %	Recov. of *m*-DCNB / %
6a (1.07)	NH_3	7	**7a**	69[d]	8	100
	$MeNH_2$	9	**7b**	67	9	67
	$EtNH_2$	9	**7c**	67	2	88
	$PrNH_2$	9	**7d**	40	5	74
	i-$PrNH_2$	9	**7e**	56	16	79
	CH_2=$CHCH_2NH_2$	8	**7f**	83	2	66
6b (1.08)	NH_3	8	**7g**	62	1	89
	$MeNH_2$	7	**7h**	59	12	90
	$EtNH_2$	10	**7i**	55	25	82
	i-$PrNH_2$	7	**7j**	61	33	98
6c (1.04)	$MeNH_2$	10	**7k**	64	7	78
6d (1.09)	$MeNH_2$	10	**7l**	60	7	83
	$EtNH_2$	12	**7m**	76	6	81
	$PrNH_2$	10	**7n**	68	4	87
	i-$PrNH_2$	10	**7o**	71	6	87

[a] For an acetonitrile-water (9:1; 100 mL) solution containing ArH (10 mmol), DCNB (5 mmol), and an amine (100 mmol). [b] Half-peak oxidation potentials vs. $Ag/AgNO_3$ [c] Isolated yields based on ArH used. [d] Values from Chapter 2.

they were easily isolated as following procedure: After evaporation of acetonitrile, the photolysates were dissolved in benzene and then extracted with dilute aq. HCl. Aqueous layer was neutralized with aq $NaHCO_3$ and extracted with Et_2O to give aminated products. DCNB was almost recovered from the benzene solution. The results were summarized in Table 3. It was confirmed that no photoamination occurred in the absence of *m*-DCNB. Moreover, it should be noted that the amino group was selectively introduced into C-1 position of naphthalene ring and no other isomers such as 1-amino-2-alkoxy-1,2-dihydro-naphthalenes formed at all.



6 7

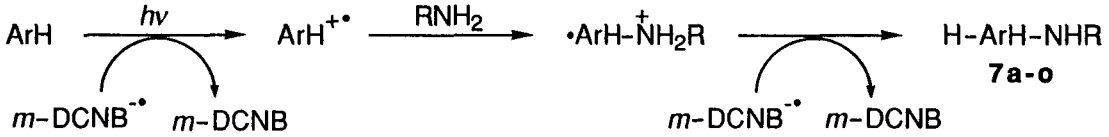
	R^1
6a	Me
6b	Et
6c	*i*-Bu
6d	CH_2Ph

	R^1	R^2
7a	Me	H
7b	Me	H
7c	Me	H
7d	Me	H
7e	Me	H
7f	Me	Allyl
7g	Et	H
7h	Et	Me

	R^1	R^2
7i	Et	Et
7j	Et	Et
7k	*i*-Bu	Me
7l	CH_2Ph	Me
7m	CH_2Ph	Et
7n	CH_2Ph	Pr
7o	CH_2Ph	*i*-Pr

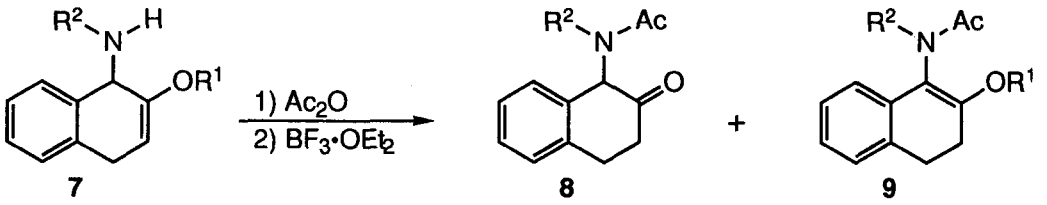
Scheme 2.

As has been reported for the photoamination of **6** with ammonia in Chapter 2, the photoamination of 2-alkoxynaphthalenes (ArH) certainly initiated by photochemical electron transfer from ArH to *m*-DCNB, since no photoamination of ArH in the absence of *m*-DCNB occurred and the oxidation potentials of ArH were relatively low (Table 1). Nucleophilic addition of an alkylamine to the resulting cation radical of ArH afforded the aminated cation radicals which were reduced by the anion radical of *m*-DCNB and then protonated to give AADN, as shown in Scheme 3. Therefore, the regioselective amination on C-1 position of naphthalene ring can be attributed to the distribution of positive charge on the cation radicals of ArH. Although the steric repulsion between alkylamino group and alkoxy group are predicted, the alkylamines selectively attack at C-1 where the highest positive charge might develop. This is accord with the addition of CN^-,[10] BH_4^-,[11] and ammonia which took place at C-1 position of the cation radical of **6**.



Scheme 3

Preparation of 1-Amino-2-tetralones. If the dealkylation of vinyl ether moiety easily takes place in AADN, these can lead to 1-alkylamino-2-tetralones in a similar manner to the preparation of 2-tetralone by Birch reduction of 2-ethoxynaphthalene followed by hydrolysis.[12] The dealkylation reactions were performed at room temperature, since AADN decomposed to the parent alkoxynaphthalenes at elevated temperature, as reported for 9-amnio-9,10-dihydrophenanthrene derivatives.[13] The dealkylation by mineral acids such as H_2SO_4, H_3PO_4, and CF_3SO_3H did not occur at room temperature. 1-Amino-2-methoxy-1,4-dihydronaphthalene **6e** was acetylated with Ac_2O and then treated with excess BF_3·OEt_2 at room temperature to give 1-acetylamino-2-tetralone **8a** in 92 % yield (entry 1). BF_3·OEt_2 was most effective among Lewis acid investigated (e.g. BF_3 gas and $AlCl_3$). But direct treatment of compound **5** with BF_3·OEt_2 gave 2-naphthol and/or intractable materials. Also, usual treatment of benzyloxy compound with Pd/C under hydrogen atmosphere did not cause debenzylation. The results are summarized in Table 4 and Scheme 4.



7 **8** **9**

	R^1
8a	H
8b	Allyl
8c	Me
8d	Et
8e	*i*-Pr

	R^1	R^2
9a	Me	Me
9b	Me	Et
9c	Me	Pr
9d	Me	*i*-Pr
9e	Et	Me
9f	*i*-Bu	Me
9g	CH_2Ph	Et

Scheme 4.

Table 4. Treatment of The Acetamides of AADN with $BF_3 \cdot OEt_2$[a]

Entry	Acetamides of AADN		Products (Yield[b] / %)			
	R^1	R^2				
1	Me	H	**8a**	92		
2	Me	Allyl	**8b**	55		
3	Me	Me	**8c**	80	**9a**	9
4	Me	Et	**8d**	49	**9b**	12
5	Me	Pr			**9c**	42
6	Me	*i*-Pr			**9d**	86
7	Et	Me	**8c**	75	**9e**	12
8	*i*-Bu	Me	**8c**	47	**9f**	40
9	CH_2Ph	Me	**8c**	77		
10	CH_2Ph	Et	**8d**	49	**9g**	42
11	CH_2Ph	*i*-Pr	**8e**	40		

[a] Reaction of the acetamide of AADN (2 mmol) with $BF_3 \cdot OEt_2$ (5-10 mL) at room temperature for 3-10 h. [b] Isolated yields based on AADN used.

Similarly, *N*-acetyl-1-allylamino-2-tetralone **8a** was readily prepared by the treatment of the acetamide of 1-allylamino-2-methoxy-1,4-dihydronaphthalene **8b** without the reaction of vinyl group (entry 2). However, the treatment of the acetamides of **7b** and **7c** (R^1 = Me and R^2 = Me and Et) with $BF_3 \cdot OEt_2$ gave mixtures of *N*-acetyl-1-alkylamino-2-tetralones, **8c** and **8d**, and small amounts of the isomerized products, *N*-acetyl-1-alkylamino-2-methoxy-3,4-dihydro-naphthalenes **9a** and **9b**, respectively (entries 3 and 4). In the cases of R^1 = Me and R^2 = Pr and i-Pr (**7d** and **7e**), only isomerization occurred, affording **9c** and **9d**, respectively (entries 5 and 6). In order to improve the yields of *N*-acetyl-1-methylamino-2-tetralone **8b**, the acetamides of several AADN (R^1 = Et, *i*-Bu, CH_2Ph, R^2 = Me) were treated with $BF_3 \cdot OEt_2$. The treatment of the acetamides of 2-ethoxy- and 2-isobutoxy-1-methylamino-1,4-dihydronaphthalenes, **7h** and **7k**, gave mixtures of 1-methylamino-2-tetralone **8b** and the isomerized product **9e** and **9f** (entries 7 and 8), while the treatment of the acetamide of 2-

benzyloxy-1-methylamino-1,4-dihydronaphthalene **7l** gave only compound **8c** in 77% yield (entry 9).

Also *N*-acetyl-1-isopropylamino-2-tetralones **8e** was prepared by the debenzylation of the acetamides of 1-isopropylamino-2-benzyloxy-1,4-dihydronaphthalenes **7o** (entry 11), but *N*-acetyl-1-propylamino-2-tertalone could not be prepared from the corresponding amides. Thus, it was found that benzyl group was more suitable as R^1 for the preparation of 1-amino-2-tetralones, since the yields of both the photoamination and the dealkylation were relatively high.

Although 1-amino-2-tetralones are pharmaceutically useful intermediate,[14] no convenient methods have been reported so far, compared with the case of the analogous 2-amino-1-tetralones.[15] Thus, the photoamination and subsequent dealkylation will become a convenient method to prepare 1-amino-2-tetralones from commercially available starting materials.

4-2-3 Experimental

M.p.s were measured on a Shibata MEL 270 melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were taken for $CDCl_3$ solutions on a Bruker AC-250P spectrometer. A Hitachi M-2000A was used for analysing the mass spectra. Oxidation potentials were measured in acetonitrile on a Hokuto Denko HA-501G potentiostat and a HB-105 function generator, using $Ag/AgNO_3$ as reference electrode. GLC analysis were performed on a Shimadzu GC-14A using a capillary column (CBP1-M25-025).

Spectral-grade acetonitrile was distilled from P_2O_5 and then from CaH_2. 2-Methoxy-, 2-ethoxy-, and 2-isobutoxynaphthalenes **6a-c** and m-dicyanobenzene were commercially available. 2-Benzyloxynaphthalene **6d** was prepared by refluxing aqueous solution of 2-naphthol with benzyl bromide in the presence of K_2CO_3 and tetrabutylammonium chloride. ***6d***: Mp 96-98 °C (from methanol) (lit.[16] 101.5-102 °C); ^1H NMR ($CDCl_3$, 250 MHz) δ = 5.18 (2H, s), 7.22-7.50 (9H, m), and 7.70-7.77 (3H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 70.01, 107.28, 119.04, 123.69, 126.36, 126.78, 127.57, 127.64, 128.00, 128.30, 128.50, 129.44, 135.02, 137.25, and 157.65.

General Procedure of Photoamination. The photoaminations of 2-alkoxynaphthalenes **6** were carried out by irradiating a deaerated acetonitrile-water (9:1 V/V; 100mL) solution containing the arene (10 mmol), *m*-DCNB (2.5 mmol), and an amine (50 mmol) by high-pressure mercury lamp through a Pyrex filter. A general procedure for isolation of AADN is as follows: After evaporation of acetonitrile, the photolysates were dissolved in benzene and then extracted with dilute HCl and neutralized with aq $NaHCO_3$. The AADN were isolated from aqueous layer after extraction of the solution with Et_2O. The starting arene and *m*-DCNB were recovered from benzene solution. The acetylation of AADN was performed with Ac_2O in pyridine.

*1-Amino-2-methoxy-1,4-dihydronaphthalene (**7a**)*:[2] ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 28.93, 50.62, 54.37, 91.38, 126.28, 126.72, 127.82, 128.73, 133.96, and 137.56.

*2-Methoxy-1-methylamino-1,4-dihydronaphthalene (**7b**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 2.06 (3H, s), 2.65 (1H, br s), 3.33-3.64 (2H, m), 3.64 (3H, s), 4.41 (1H, t, J = 3.2 Hz), 5.08 (1H, dd, J = 4.6 and 3.0 Hz), 7.15-7.26 (3H, m), and 7.45 (1H, d, J = 8.5 Hz); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 29.11, 29.65, 54.40, 57.07, 94.46, 126.16, 126.67, 127.58, 128.89, 135.06, 135.77, and 152.66; *m/z* 189 (M^+). The acetamide; Found: M^+ 231.1224. Calcd. for $C_{14}H_{17}NO_2$: M, 231.1258; *m/z* 231 (M^+), 188 (M-Ac), and 158.

*1-Ethylamino-2-methoxy-1,4-dihydronaphthalene (**7c**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.96 (1H, br s), 1.04 (3H, t, J = 7.1 Hz), 2.23 (1H, m), 2.46-2.59 (1H, m), 3.31-3.43 (1H, m), 3.50-3.71 (1H, m), 3.63 (3H, s), 4.48 (1H, s), 5.06 (1H, dd, J = 4.6 and 2.9 Hz), 7.15-7.30 (3H, m), and 7.53 (1H, d, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 14.86, 29.13, 38.07, 54.46, 56.60, 94.62, 126.20, 126.88, 127.67, 129.07, 134.76, 135.79, and 152.81; *m/z* 203 (M^+). The acetamide; Found: M^+ 245.1382. Calcd. for $C_{15}H_{19}NO_2$: M, 245.1414, *m/z* 245 (M^+), 202 (M-Ac), and 158.

*2-Methoxy-1-n-propylamino-1,4-dihydronaphthalene (**7d**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.81 (3H, t, J = 7.4 Hz), 7.29 (2H, hex, J = 7.3 Hz), 2.05-2.15 (1H, m), 2.20 (1H, br s), 2.31-2.41 (1H, m), 3.32-3.64 (2H, m), 3.64 (3H, s), 4.42 (1H, t, J = 3.2 Hz), 5.04 (1H, t, J = 3.1 Hz), 7.18-7.26 (3H, m), and 7.46-7.49 (1H, m); ^{13}C NMR ($CDCl_3$, 250

MHz) δ = 11.86, 23.43, 29.12, 45.48, 54.28, 56.47, 93.80, 126.04, 126.50, 127.57, 128.85, 135.56, 135.95, and 153.58; *m/z* 217 (M^+). The acetamide; Found: M^+ 259.1556. Calcd. for $C_{16}H_{21}NO_2$: M, 259.1571; *m/z* 259 (M^+), 216 (M-Ac), and 158.

*1-Isopropylamino-2-methoxy-1,4-dihydronaphthalene (**7e**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.89 (3H, d, *J* = 6.3 Hz), 1.02 (3H, d, *J* = 6.3 Hz), 1.94 (1H, br s), 2.88 (1H, sept, *J* = 6.3 Hz), 3.29-3.40 (1H, m), 3.50-3.60 (1H, m), 3.60 (3H, s), 4.33 (1H, t, *J* = 2.8 Hz), 4.93-4.97 (1H, m), 7.06-7.26 (3H, m), and 7.36-7.39 (1H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 23.79, 23.89, 29.02, 45.18, 54.29, 55.41, 93.09, 125.89, 126.40, 127.74, 128.94, 135.40, 137.30, and 155.92; *m/z* 217 (M^+). The acetamide; mp 119-120°C; Found C, 74.15; H, 8.34; N, 5.55. Calcd. for $C_{16}H_{21}NO_3$: C, 74.10; H, 8.16; N, 5.40.

*1-Allylamino-2-methoxy-1,4-dihydronaphthalene (**7f**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 2.00 (1H, br s), 2.82 (1H, dd, *J* = 13.6 and 5.8 Hz), 3.05 (1H, dd, *J* = 13.6 and 6.3 Hz), 3.34-3.62 (2H, m), 3.62 (3H, s), 4.42 (1H, t, *J* = 3.2 Hz), 4.96-5.12 (2H, m), 5.74-5.90 (1H, m), 7.16-7.24 (3H, m), and 7.44-7.48 (1H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 29.11, 46.67, 54.34, 56.13, 93.88, 115.30, 126.08, 126.58, 127.58, 128.92, 135.56, 135.82, 137.41, and 153.69. The acetamide; Found: M^+ 257.1414. Calc. for $C_{16}H_{19}NO_2$: M, 257.1384.

*1-Amino-2-ethoxy-1,4-dihydronaphthalene (**7g**)*: The acetamide; mp 174-176°C (from methanol); ^1H NMR ($CDCl_3$, 250 MHz) δ = 1.31 (3H, d, *J* = 6.9 Hz), 2.00 (3H, s), 3.38-3.59 (2H, m), 3.74-3.84 (2H, m), 5.00 (1H, t, *J* = 3.5 Hz), 5.74-5.82 (1H, m), 7.17-7.30 (3H, m), and 7.43-7.46 (1H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 14.56, 23.40, 28.82, 47.91, 62.57, 94.98, 126.55, 127.11, 127.66, 128.90, 134.09, 135.70, 151.58, and 169.83; Found: C, 72.40; H, 7.14; N, 5.82. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06.

*2-Ethoxy-1-methylamino-1,4-dihydronaphthalene (**7h**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 1.34 (3H, d, *J* = 7.0 Hz), 2.07 (3H, s), 3.13 (1H, br s), 3.37 (1H, dt, *J* = 21.0 and 3.7 Hz), 3.54 (1H, dt, *J* = 21.0 and 3.1 Hz), 3.82 (2H, q, *J* = 7.0 Hz), 4.40 (1H, t, *J* = 3.3 Hz), 5.05 (1H, dd, *J* = 4.6 and 3.1 Hz), 7.12-7.25 (3H, m), and 7.44-7.47 (1H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 14.66, 29.20, 29.50, 57.13, 62.32, 94.97, 126.18, 126.73,

127.58, 129.00, 134.80, 135.89, and 151.66; *m/z* 203 (M^+). The acetamide; Found: M^+ 245.1374. Calcd. for $C_{15}H_{19}NO_2$: M, 245.1414; *m/z* 245 (M^+), 202 (M-Ac), and 172.

2-Ethoxy-1-ethylamino-1,4-dihydronaphthalene (7i): Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 1.00 (3H, t, J = 7.2 Hz), 1.34 (3H, t, J = 7.0 Hz), 2.20-2.30 (2H, m), 2.44-2.57 (2H, m), 2.59 (1H, br s), 3.36 (1H, dt, J = 21.1 and 4.5 Hz), 3.55 (1H, dt, J = 21.1 and 3.2 Hz), 3.82 (2H, q, J = 7.0 Hz), 4.39 (1H, t, J = 3.3 Hz), 5.00 (1H, dd, J = 4.7 and 3.0), 7.16-7.25 (3H, m), and 7.45-7.49 (1H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 14.68, 15.48, 29.23, 38.20, 56.81, 62.28, 94.17, 126.03, 126.52, 127.06, 128.96, 135.67, 136.06, and 153.00; *m/z* 217 (M^+). The acetamide; Found: M^+, 259.1558. Calcd. for $C_{16}H_{21}NO_2$: M, 259.1570; *m/z* 259 (M^+), 216 (M-Ac), 188 (M-Ac-C_2H_4), and 172.

2-Ethoxy-1-isopropylamino-1,4-dihydronaphthalene (7j): Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.88 (3H, d, J = 6.2 Hz), 1.04 (3H, d, J = 6.2 Hz), 1.33 (3H, t, J = 7.0 Hz), 2.06 (1H, br s), 2.93 (1H, sept, J = 6.2 Hz), 3.34 (1H, ddd, J = 20.9, 5.1, and 2.6 Hz), 3.56 (1H, dt, J = 20.9 and 2.8 Hz), 3.79 (2H, q, J = 7.0 Hz), 4.32 (1H, t, J = 2.9 Hz), 4.93 (1H, dd, J = 5.1 and 2.8 Hz), 7.13-7.23 (3H, m), and 7.39-7.42 (1H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 14.68, 23.85, 23.99, 29.10, 45.51, 55.56, 62.17, 93.38, 125.91, 126.36, 127.67, 129.03, 135.41, 137.52, and 155.07; *m/z* 231 (M^+). The acetamide; Found: M^+ 273.1710. Calcd. for $C_{17}H_{23}NO_2$: M, 273.1727).

2-Isobutoxy-1-methylamino-1,4-dihydronaphthalene (7k): Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.98 (3H, d, J = 6.6 Hz), 0.99 (3H, d, J = 6.6 Hz), 2.06 (3H, s), 2.42 (1H, br s), 3.32-3.58 (5H, m), 4.40 (1H, t, J = 3.4 Hz), 5.02 (1H, dd, J = 4.5 and 3.2 Hz), 7.13-7.26 (3H, m), and 7.45-7.49 (1H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 19.39, 28.07, 29.21, 29.83, 57.12, 73.26, 94.40, 126.08, 126.53, 127.50, 129.00, 135.43, 135.77, and 52.23; *m/z* 231 (M^+). The acetamide; Found: M^+, 273.1733. Calcd. for $C_{17}H_{23}NO_2$: M, 273.1727.

2-Benzyloxy-1-methylamino-1,4-dihydronaphthalene (7l): Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 2.07 (3H, s), 2.38 (1H, br s), 3.38 (1H, dt, J = 21.2 and 4.0 Hz), 3.55 (1H, dt, J = 21.2 and 3.2 Hz), 4.47 (1H, t, J = 3.4 Hz), 4.84 (2H, s), 5.15 (1H, dd, J = 4.6 and 3.2 Hz), and 7.12-7.48 (9H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 29.16, 29.75, 57.04, 68.90,

95.71, 126.12, 126.58, 127.39, 127.47, 127.76, 128.44, 128.98, 135.24, 135.58, 137.28, and 151.90; *m/z* 265 (M^+). *The acetamide;* Found: M^+ 307.1549. Calcd. for $C_{20}H_{21}NO_2$: M, 307.1570.

*1-Ethylamino-2-benzyloxy-1,4-dihydronaphthalene (**7m**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.99 (3H, t, J = 7.1 Hz), 2.03-2.28 (1H, m), 2.33 (1H, br s), 2.44-2.54 (1H, m), 3.36 (1H, dt, J = 21.1 and 4.2 Hz), 3.54 (1H, dt, J = 21.0 and 3.1 Hz), 4.48 (1H, t, J = 3.3 Hz), 4.83 (2H, s), 5.10 (1H, dd, J = 4.5 and 3.1 Hz), and 6.95-7.50 (9H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 15.67, 29.29, 38.13, 56.71, 69.98, 95.29, 126.18, 126.62, 127.47, 127.63, 127.86, 128.56, 128.56, 129.06, 135.48, 136.06, 137.45, and 152.86. The acetamide; Found: M^+, 321.1739. Calcd. for $C_{21}H_{23}NO_2$: M^+, 321.1727.

*2-Benzyloxy-1-propylamino-1,4-dihydronaphthalene (**7n**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.81 (3H, t, J = 7.4 Hz), 1.35-1.47 (2H, m), 2.11-2.21 (1H, m), 2.35-2.46 (1H, m), 3.39 (1H, dt, J = 21.3 and 3.7 Hz), 3.57 (1H, dt, J = 27.7 and 3.3 Hz), 4.62 (1H, t, J = 3.5 Hz), 4.86 (2H, s), 5.16 (1H, dd, J = 4.5 and 3.3 Hz), 5.45 (1H, br s), and 7.16-7.54 (9H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 11.83, 22.89, 29.20, 45.02, 56.12, 69.01, 96.08, 126.32, 126.90, 127.44, 127.44, 127.66, 127.86, 128.52, 128.52, 129.06, 134.60, 135.48, 137.20, and 151.59; m/z 293 (M^+). The acetamide; Found: M^+ 335.1848. Calcd. for $C_{22}H_{25}NO_2$: M, 335.1883.

*2-Benzyloxy-1-isopropylamino-1,4-dihydronaphthalene (**7o**)*: Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.86 (3H, d, J = 6.2 Hz), 1.06 (3H, d, J = 6.2 Hz), 2.00 (1H, br s), 2.90-3.06 (1H, m), 3.39 (1H, dt, J = 20.1 and 2.2 Hz), 3.58 (1H, dt, J = 20.0 and 2.1 Hz), 4.42 (1H, t, J = 3.3 Hz), 4.86 (2H, s), 4.06 (1H, dd, J = 4.8 and 2.8 Hz), and 7.15-7.43 (9H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 23.58, 23.82, 28.80, 45.32, 55.14, 68.58, 94.17, 125.73, 126.13, 127.06, 127.06, 127.38, 127.38, 128.13, 128.13, 128.79, 134.17, 137.04, 137.18, and 154.67; *m/z* 293 (M^+). The acetamide; Found: M^+ 335.1848. Calcd. for $C_{22}H_{25}NO_2$: M, 335.1883

Treatment of The Acetamide of AADN (7) with $BF_3 \cdot OEt_2$. A solution of $BF_3 \cdot Et_2O$ (10 mL) of the acetamide of AADN (2 mmol) was stirred at room temperature for 3-10 h. After

neutralization with aqueous Na_2CO_3 solution, the solution was extracted with diethyl ether. Then evaporation of the ether left the crude *N*-acetyl-1-amino-2-tetralones and/or *N*-acetyl-2-alkoxy-1-alkylamino-3,4-dihydronaphthalenes. The isolation of *N*-acetyl-1-alkylamino-2-tetralones was performed by column chromatography on silica gel.

*N-Acetyl-1-aminotetralone (**8a**)*: Mp 175-178 °C; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 2.22 (3H, s), 2.37-2.52 (1H, m), 2.75-2.86 (2H, m), 2.96-3.05 (1H, m), 3.21-3.31 (1H, m), 5.65 (1H, d, J = 12.0 Hz), 6.54 (1H, br s), and 7.04-7.27 (4H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 25.13, 27.11, 35.37, 59.47, 124.22, 127.29, 127.37, 127.70, 133.46, 136.27, 170.86, and 206.41; Found C, 71.07; H, 6.67; N, 6.97. Calcd. for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89.

*N-Acetyl-N-allyl-1-aminotetralone (**8b**)*: Oil; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 2.20 (3H, s), 2.49-3.17 (4H, m), 3.83-4.15 (2H, m), 5.01-5.26 (2H, m), 5.43 (1H, s), 5.77-5.99 (1H, m), and 7.07-7.46 (4H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 21.66, 28.32, 38.25, 52.84, 63.96, 118.41, 126.18, 126.91, 127.40, 128.02, 133.81, 134.84, 136.59, 171.27, and 205.56; Found: M^+, 243.1217. Calcd. for $C_{15}H_{17}NO_2$: M, 243.1257.

*N-Acetyl-N-methyl-1-aminotetralone (**8c**)*: Oil; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 2.24 (3H, s), 2.37-2.59 (2H, m), 2.72-2.97 (4H, m), 2.84 (3H, s), 3.01-3.35 (1H, m), 6.32 (1H, s), and 6.92-7.35 (4H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 21.34, 28.34, 34.30, 37.79, 63.59, 125.96, 126.89, 127.60, 128.06, 133.34, 136.85, 172.31, and 205.66; Found: M^+, 217.1143. Calcd. for $C_{13}H_{15}NO_2$: M, 217.1101.

*N-Acetyl-N-ethyl-1-aminotetralone (**8d**)*: Oil; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 1.25 (3H, t, J = 7.1 Hz), 2.18 (3H, s), 2.54-3.44 (6H, m), 5.12 (1H, s), and 6.94-7.53 (4H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 14.72, 21.09, 28.28, 38.15, 45.32, 64.45, 125.91, 126.82, 127.02, 127.99, 134.88, 136.37, 173.60, and 205.59; (Found: M^+, 231.1246. Calcd. for $C_{14}H_{17}NO_2$: M, 231.1288).

*N-Acetyl-N-isopropyl-1-aminotetralone (**8e**)*: Oil; ^{1}H NMR ($CDCl_3$, 250 MHz) δ = 1.30 (3H, d, J = 6.6 Hz), 1.35 (3H, d, J = 6.6 Hz), 2.18 (3H, s), 2.42-3.08 (4H, m), 3.80-3.95 (1H, m), 4.43 (1H, s), and 6.90-7.32 (4H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 21.58,

21.66, 22.15, 27.92, 36.88, 47.46, 60.13, 126.36, 126.62, 127.09, 128.39, 132.41, 135.73, 173.35, and 205.98; Found: M^+, 245.1410. Calcd. for $C_{15}H_{19}NO_2$: M, 245,1416.

Since the isomerized products (**9**) could not be purified, the spectral data were measured as mixture with the corresponding 1-amino-2-tetralones except for the cases of **9c** and **9d**.

N-Acetyl-1-methylamino-2-methoxy-3,4-dihydronaphthalene (***9a***): ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 20.99, 26.95, 27.12, 37.70, 55.28, 118.68, 126.92, 127.56, 127.64, 128.33, 132.99, 133.44, 152.36, and 173.73; *m/z* 231 (M^+).

N-Acetyl-1-ethylamino-2-methoxy-3,4-dihydronaphthalene (***9b***): ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 12.88, 22.64, 27.85, 27.91, 43.19, 55.25, 120.08, 124.91, 126.80, 126.96, 127.02, 132.29, 133.11, 153.69, and 172.31; *m/z* 245 (M^+).

N-Acetyl-2-methoxy-1-n-propylamino-3,4-dihydro-naphthalene (***9c***): Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ =0.87 (3H, t, *J* = 7.4 Hz), 1.43-1.62 (2H, m), 1.90 (3H, s), 2.53-2.61 (1H, m), 2.66-2.71 (2H, m), 2.89-2.97 (2H, m), 3.72 (3H, s), 3.80-3.92 (2H, m), and 6.95-7.28 (4H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 11.51, 21.14, 21.24, 22.62, 26.90, 47.98, 55.19, 117.96, 121.07, 125.75, 126.98, 127.21, 132.37, 133.09, 153.58, and 172.24; Found: M^+ 259.1549. Calcd. for $C_{16}H_{21}NO_2$: M, 259.1570.

N-Acetyl-2-methoxy-1-isopropylamino-3,4-dihydro-naphthalene (***9d***): Oil; ^1H NMR ($CDCl_3$, 250 MHz) δ = 0.95 (3H, d, *J* = 6.8 Hz), 1.12 (3H, d, *J* = 6.5 Hz), 1.84 (3H, s), 2.36-2.49 (1H, m), 2.71 (1H, ddd, *J* = 16.6, 6.4, and 3.7 Hz), 2.87-3.03 (2H, m), and 6.99-7.25 (4H, m); ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 20.62, 20.73, 22.01, 22.91, 27.97, 47.24, 55.08, 115.29, 121.90, 125.46, 126.67, 126.89, 131.94, 135.03, 155.05, and 172.18; Found: M^+ 259.1620. Calcd. for $C_{16}H_{21}NO_2$: M, 259.1572.

N-Acetyl-1-methylamino-2-ethoxy-3,4-dihydronaphthalene (***9e***): ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 14.81, 21.02, 23.42, 27.73, 27.90, 34.40, 118.96, 126.58, 127.07, 132.43, 133.05, 152.45, and 173.69; *m/z* 245 (M^+).

N-Acetyl-1-methylamino-2-isobutyloxy-3,4-dihydro-naphthalene (***9f***): ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 19.08, 19.08, 20.91, 23.51, 27.90, 28.83, 34.32, 74.59, 119.69, 121.34, 125.95, 127.06, 127.21, 132.15, 133.04, 152.83, and 172.50; *m/z* 273 (M^+).

*N-Acetyl-2-benzyloxy-1-ethylamino-3,4-dihydronaphthalene (**9g**)*: Oil; ^{13}C NMR ($CDCl_3$, 250 MHz) δ = 12.82, 21.55, 27.84, 28.22, 40.93, 65.01, 120.05, 124.91, 125.83, 126.80, 127.32, 127.42, 127.42, 128.02, 128.44, 128.44, 132.51, 133.47, 134.79, 153.32, and 173.59. Found: M^+ 321.1752. Calcd. for $C_{21}H_{23}NO_2$: M, 321.1728

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Conclusion

The results obtained from the present investigation are summarized as follows;

Chapter 1: Photoinduced nucleophilic addition of ammonia and alkylamines to 1,1-diphenylpropene and 1,1-diphenylethene with gave the corresponding *N*-substituted 2-amino-1,1-diphenylpropane and *N*-substituted 1-amino-2,2-diphenylethane, respectively, along with the formation of considerable amounts of acetonitrile-incorporated products.

The regiochemistry on photoaddition of ammonia to 1-aryl-2-phenylethenes was investigated. The photoamination of 1-aryl-2-phenylethenes having an alkoxy group on the para position occurred selectively to give 1-amino-2-aryl-1-phenylethane. On the other hand, the photoamination of 1-aryl-2-phenylethenes having a methyl and chloro group on the para position or methoxy group on the meta and ortho positions gave both 1-amino-2-aryl-1-phenylethane and 1-amino-1-aryl-2-phenylethane. The regiochemistry is related with the distribution of positive charge in the cation radicals of substrates generated from photoinduced electron transfer to dicyanobenzene.

Photoamination of styrene derivatives in the presence of *m*-dicyanobenzene (*m*-DCNB) gave phenethylamine derivatives. Also, an improvement of the yield of the aminated products was achieved by the addition of 1,3,5-triphenylbenzene or *m*-terphenyl.

Chapter 2: The photoamination of phenathrene, 9-methoxyphenathrene, anthracene, naphthalene, and several substituted naphthalenes with ammonia or primary amines in the presence of *m*-DCNB gave aminated dihydroarenes in fairly good yields. Also, bifunctional alkylamines containing the vinyl, cyano, hydroxy, acetylamino and ethoxycarbonyl groups can be efficiently used as amination reagents that do not react with the other functional groups at all. These photoaminations proceed by nucleophilic addition of amine to the cation radicals generated from photochemical electron transfer to *m*-DCNB to form the aminted cation radicals

which underwent the reduction by the anion radical of *m*-DCNB, followed by a protonation to give final products.

The photoamination of 9-alkoxyphenanthrene with alkylamine formed mainly cis-9-alkoxy-10-alkylamino-9,10-dihydrophenathrenes, showing that the selective trans addition of amines occurred. This arise from the protonation the conformation of the aminated anions.

Chapter 3: 9,10-Dicyanoanthracene (DCA)- or 9-cyanoanthracene-sensitized photooxygenation of *trans*-stilbene derivatives gave benzaldehyde derivatives efficiently in the presence of weak-nucleophilic salts such as Et_4NOAc and KOAc/18-crown-6 ether. The product distribution of this photooxygenation was apparently different from that of each photooxygenation in the presence of $Mg(ClO_4)_2$ and Et_4NBF_4 or in the absence of the salt. The DCA-sensitized photooxygenation of 2-methylnaphthalene gave phthalic acid and 4-methylphthalic acid in the presence of Et_4NOAc. These products were different from the products generated from each photooxygenation in the presence of Et_4NBF_4 and $KClO_4$ or in the absence of the salt. Thus, the present investigation reveals that the reaction courses of photooxygenation via electron transfer can be controlled by the use of non- or weak-nuleophilic salts, as well as by the choice of solvents.

Chapter 4: Direct phosphonations of naphthalene and phenanthrene can be achieved by the photoreaction of the arenes with trialkyl phosphites in the presence of *m*-DCNB to give arylphosphonates and dihydroarylphosphonates. The author applied the photoamination of 2-alkoxynaphthalenes to the synthesis of 1-alkylamino-tetralones having medicinal interests. A convenient method for synthesis of 1-alkylamino-tetralones has been developed by preparation from commercially available starting materials.

List of Publications

1) Synthetic Application of Photochemical Electron Transfer to Direct Amination of Arenes by Ammonia and Primary Amines
M. Yasuda, T. Yamashita, T. Matsumoto, K. Shima, and C. Pac
J. Org. Chem., **50**, 3667 (1985).

2) Direct Photoamination of Arenes with Ammonia and Primary Amines in the Presence of Electron Acceptors
M. Yasuda, T. Yamashita, K. Shima, and C. Pac
J. Org. Chem., **52**, 753 (1987).

3) Direct Phoshonation of Naphthalene and Phenanthrene with Trialkyl Phosphites via Photochemical Electron Transfer
M. Yasuda, T. Yamashita, and K. Shima
Bull. Chem. Soc. Jpn., **63**, 938 (1990).

4) Photoinduced Nucleophilic Addition of Ammonia and Alkylamines to Aryl-Substituted Alkenes in the Presence of *p*-Dicyanobenzene
T. Yamashita, K. Shiomori, M. Yasuda, and K. Shima
Bull. Chem. Soc. Jpn., **64**, 366 (1991).

5) Unusual Effects of Acetate Ion on Photosensitized Oxygenation of Naphthalene Derivatives via Electron Transfer
T. Yamashita, T. Tsurusako, M. Yasuda, and K. Shima
Chem. Lett., **1991**, 1487.

6) Stereochemical Studies on the Amination of Arenes with Ammonia and Alkylamines via Photochemical Electron Transfer
M. Yasuda, K. Shiomori, S. Hamasuna, T. Yamashita, and K. Shima
J. Chem. Soc., Perkin Trans. 2, **1992**, 305.

7) Regiochemistry on Photoamination of Stilbene Derivatives with Ammonia via Electron Transfer
M. Yasuda, T. Isami, J. Kubo, M. Mizutani, T. Yamashita, and K. Shima
J. Org. Chem., **57**, 1351 (1992).

8) Electron-Transfer Photosensitized Oxygenation of Stilbene and Naphthalene Derivatives in the Presence of Acetate Ion. Controlling the Reaction of the Cation Radicals by Weak-Nucleophilic Salts
T. Yamashita, T. Tsurusako, N. Nakamura, M. Yasuda, and K. Shima
Bull. Chem. Soc. Jpn., **66**, 857 (1993).

9) A Convenient Method for Synthesis of 1-Amino-2-tetralones by Photoamination of 2-Alkoxynaphthalenes with Alkylamines
T. Yamashita, K. Yamano, M. Yasuda, and K. Shima
Chem. Lett., **1993**, 627.

10) Synthesis of Phenethylamine Moiety by Photoamination of Styrene Derivatives with Ammonia
T. Yamashita, T. Isami, S. Nakano, K. Tanabe, M. Yasuda, and K. Shima
Tetrahedron Lett., **34**, 5131 (1933).

11) Photoamination of 2-Alkoxynaphthalenes with Alkylamines via Electron Transfer and its Application to Synthesis of 1-Alkylamino-2-tetralones
T. Yamashita, K. Tanabe, K. Yamano, M. Yasuda, and K. Shima
Bull. Chem. Soc. Jpn., to be submitted.

Acknowledgment

The work described in this thesis has been carried out under the guidance by Professor Kensuke Shima and Associate Professor Masahide Yasuda, Department of Industrial Material Science, Faculty of Engineering, Miyazaki University.

The author would like to express his sincere thanks to Professor Kensuke Shima and Associate Professor Masahide Yasuda for invaluable guidance and constant encouragement that he has given throughout this investigation.

The author's grateful thanks are especially due to Professor Shinji Murai, Professor Yoshiki Ohshiro, Professor Hideo Kurosawa, and Associate Professor Naoto Chatani, Department of Applied Chemistry, Faculty of Engineering, Osaka University, for their kind discussion and suggestion.

The author is also grateful to Dr. Chyongjin Pac at Kawamura Institute of Chemical Research for helpful suggestion.

Furthermore, the author thanks Ms. Kimiko Tanabe, Dr. Kenichi Nakabayashi, Mr. Koichiro Shiomori, Mr. Takayuki Matsumoto, Mr. Manabu Mizutani, Mr. Jun-ichi Kubo, Mr. Taiji Tsurusako, Mr. Nobuya Nakamura, Mr. Shuichi Hamasuna, Mr. Toshihiro Isami, Mr. Katsuhiko Yamano, Mr. Shozo Nakano for their collaboration. Thanks are due to the Research Center for Material Analysis in Miyazaki University for spectra and analytical data.

Finally, the author would like to express his thanks to his mother Chizuko Yamashita and his late father Masaaki Yamashita for their understanding and encouragement.

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