[4-(Trifluoromethyl)phenyl]diphenylphosphine (Entry 13, Table I). The reaction was carried out with 412 mg (1.50 mmol) of 4-(trifluoromethyl)iodobenzene and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes) to give 342 mg (69%) of a colorless oil that crystallized on standing, mp 51–53 °C (lit.[44] mp 55–57 °C): ^1H NMR (270 MHz) δ 7.56 (bd, J = 8.4 Hz, 2 H), 7.42–7.29 (m, 12 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 160.61, 138.23 (d, J = 12.1 Hz), 135.57 (d, J = 20.6 Hz), 133.46 (d, J = 18.9 Hz), 128.39, 128.30–127.98 (m), 114.41 (d, J = 8.6 Hz), 55.12; ^{31}P NMR δ −4.7.

Methyl 2-(Diphenylphosphino)benzoate (Entry 14, Table I). The reaction was carried out with 414 mg (1.50 mmol) of methyl 2-iodobenzoate and 2.5 mol % of $(MeCN)_2PdCl_2$ at 60 °C. The crude product was chromatographed (silica gel, hexanes→5% ethyl acetate/hexanes) to give 309 mg (65%) of white solid, mp 97–98.5 °C (lit.[45] mp 96–97 °C): ^1H NMR (270 MHz) δ 8.05–7.99 (m, 1 H), 7.39–7.20 (m, 12 H), 6.94–6.88 (m, 1 H), 3.70 (s, 3 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 167.22, 140.59, 138.00 (d, J = 11.3 Hz), 134.19, 133.89 (d, J = 21.6 Hz), 131.73 (bs), 130.56, 128.45 (apparent t, J = 7.7 Hz), 128.10, 51.73; ^{31}P NMR δ −3.5 (lit.[45] ^{31}P NMR δ −5.1).

(4-Acetylphenyl)diphenylphosphine (Entry 15, Table I). The reaction was carried out with 299 mg (1.50 mmol) of 4-acetylbromobenzene and 2.5 mol % of $(MeCN)_2PdCl_2$ in toluene at 105 °C. The crude product was chromatographed (silica gel, hexanes→5% ethyl acetate/hexanes) to give 297 mg (65%) of white solid, mp 118–120 °C (lit.[46] mp 118–119 °C): ^1H NMR (270 MHz) δ 7.84 (d, J = 7.9 Hz, 2 H), 7.35–7.20 (m, 12 H), 2.53 (s, 3 H); for $^{13}C\{^1H\}$ NMR data, see ref 47; ^{31}P NMR δ −4.3.

4,4'-Bis(diphenylphosphino)biphenyl (Entry 16, Table I). The reaction was carried out with 1.56 g (5.00 mmol) of 4,4'-dibromobiphenyl and 5 mol % of $(MeCN)_2PdCl_2$ in toluene at 105 °C. The crude product was chromatographed (silica gel, hexanes→20% ethyl acetate/hexanes) to give 1.05 g (40%) of white solid, mp 185–186 °C (lit.[40] mp 192.5–194 °C): ^1H NMR (270 MHz) δ 7.61 (d, J = 7.3 Hz, 4 H), 7.45–7.37 (m, 24 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 140.77, 137.24 (d, J = 10.9 Hz), 136.71 (d, J = 11.3 Hz), 134.22 (d, J = 19.6 Hz), 133.81 (d, J = 19.6 Hz), 128.80, 128.57 (d, J = 6.0 Hz), 127.06 (d, J = 7.3 Hz); ^{31}P NMR δ −5.5.

1,2-Bis(diphenylphosphino)benzene. To a cooled (−78 °C) solution of 1.02 g (3.00 mmol) of (2-bromophenyl)diphenylphosphine in 30 mL of THF was added dropwise 1.7 mL (3.0 mmol) of a 1.8 M solution of n-butyllithium in hexanes. The solution was stirred at −78 °C for 30 min and then 660 mg (3.00 mmol) of chlorodiphenylphosphine was added dropwise. The solution was allowed to warm to room temperature; then chloroform was added to the solution. The organic layer was washed with water and saturated sodium chloride and then dried over magnesium sulfate. The solvents were removed under reduced pressure. The oil was dissolved in chloroform, silica gel was added, and the chloroform was removed under reduced pressure. The coated silica gel was then loaded onto the top of a silica gel packed flash column and eluted with hexanes→30% ethyl acetate/hexanes. The solvents were removed under reduced pressure to yield 1.22 g (91%) of product, mp 179–181 °C (lit.[48] mp 183–185 °C): ^1H NMR (270 MHz) δ 7.39–7.17 (m, 20 H), 7.13–7.03 (m, 4 H); $^{13}C\{^1H\}$ NMR (67.9 MHz) δ 137.26, 134.12–134.01 (m), 133.73 (t, J = 9.9 Hz), 129.03, 128.47–128.07 (m); ^{31}P NMR δ −13.2 (lit.[49] ^{31}P NMR δ −14.3).

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Direct Photoamination of Arenes with Ammonia and Primary Amines in the Presence of Electron Acceptors[1]

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Direct photoamination of phenanthrene, 9-methoxyphenanthrene, anthracene, naphthalene, and several substituted naphthalenes with ammonia or primary amines in the presence of *m*-dicyanobenzene occurs to give aminated dihydroarenes in fairly good yields. *m*-Dimethoxybenzene and biphenyl are photoaminated in lower yields. A suggested mechanism for the photoamination involves the nucleophilic attack of ammonia and amines on aromatic cation radicals generated by photochemical electron transfer to *m*-dicyanobenzene. The present photoamination is applied to direct introduction of various functionalized primary amines containing the vinyl, cyano, hydroxy, acetylamino, and ethoxycarbonyl groups.

Photochemical electron transfer has received much attention as a convenient method for generation of ion radicals, thus having potential application to organic synthesis.[2] To apply photochemical electron transfer synthetically, we have extensively explored the possibility

(1) Photochemical Reactions of Aromatic Compounds. Part 43. For Part 42, see: Pac, C.; Ohtsuki, T.; Shiota, Y.; Yanagida, S.; Sakurai, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1133–1139.

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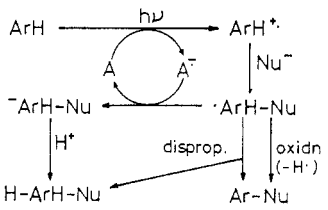
Table I. Photoamination of Phenanthrene (1a) with Ammonia or Primary Amines[a]

run	RNH_2	irradn time, h	product (yield, %)[b]	convn 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	**2h** (85)	79	35
12	$NCCH_2CH_2NH_2$	14	**2i** (66)	71	57
13	$HOCH_2CH_2NH_2$	24	**2j** (82)	76	40
14	$H_2NCH_2CH_2NH_2$	15	**2k** (95)	58	67
15	$AcNHCH_2CH_2NH_2$	18	**2l** (66)	60	63
16	$EtOCOCH_2NH_2$	16	**2m** (78)	59	94

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

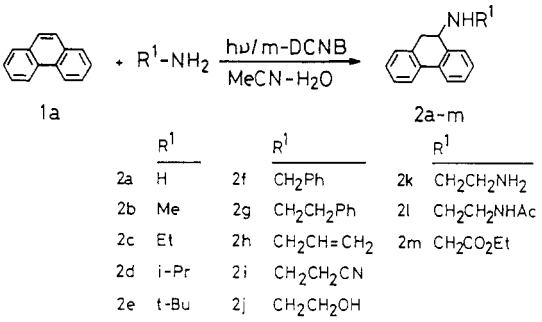
Scheme I

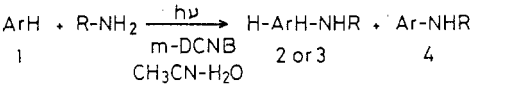


of adding nucleophiles to photogenerated cation radicals.[3] If nucleophiles efficiently add to aromatic cation radicals, useful synthetic tools can be developed to achieve the direct introduction of functional groups to aromatic nuclei (Scheme I). Indeed, a variety of arenes (ArH) are efficiently cyanated with NaCN[3a] and reduced by $NaBH_4$ upon irradiation in the presence of *p*-dicyanobenzene.

As an extension of Scheme I, we preliminarily reported the efficient direct photoamination of arenes by ammonia and primary amines (Nu = NH_2 and RNH) in the presence of *m*-dicyanobenzene (*m*-DCNB).[4] This photoamination is of synthetic significance, since direct amination of arenes is limited to Friedel–Crafts reactions with activated amination reagents or to nucleophilic addition of amide anion to highly activated arenes.[5] The preparation of aromatic amines is usually carried out by reduction of nitro, azo, and azide arenes or by substitution of halogen, hydroxy, and alkoxy groups in thermal or photochemical reactions.[5,6] Recently it was reported that substituted benzenes can be directly aminated by hydroxylamine-*O*-sulfonic acid and ferrous sulfate in acidic media.[7] 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 I seems to meet this requirement. Therefore, we have thoroughly investigated the direct photoamination of various arenes with ammonia and aliphatic amines to establish its synthetic scope and limitations.

Scheme II





Results

Photoamination of Phenanthrene (1a) with Ammonia and Primary Amines. In attempts to find optimum reaction conditions, 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 relatively efficient and clean, while methanol is a poor solvent. Moreover, photoamination yields were improved in the presence of water, as is shown in Table I. Therefore, we used 9:1 acetonitrile–water as solvent throughout the present investigation. As the electron acceptor, *m*-DCNB was generally 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 (DCNA) were found to be effective in the photoamination of *m*-dimethoxybenzene (**1l**) and biphenyl (**1m**), respectively.

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 I and Scheme II, photoamination was successfully achieved with ammonia and a wide variety of primary amines and gave selectively 9-amino- or 9-(alkylamino)-9,10-dihydrophenanthrenes **2a–n** in fairly good yields, whereas *m*-

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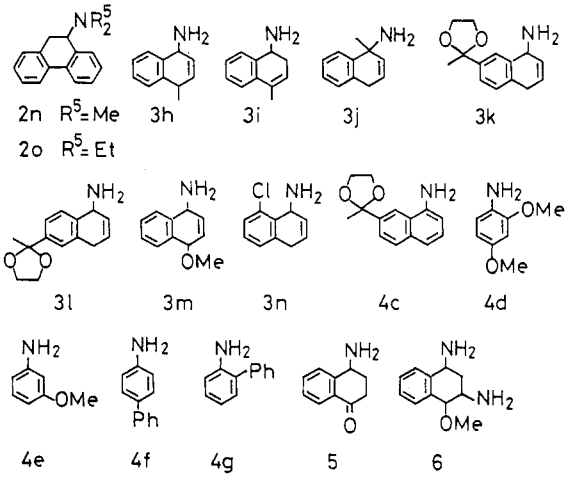
Table II. Photoamination of Arenes with Ammonia[a]

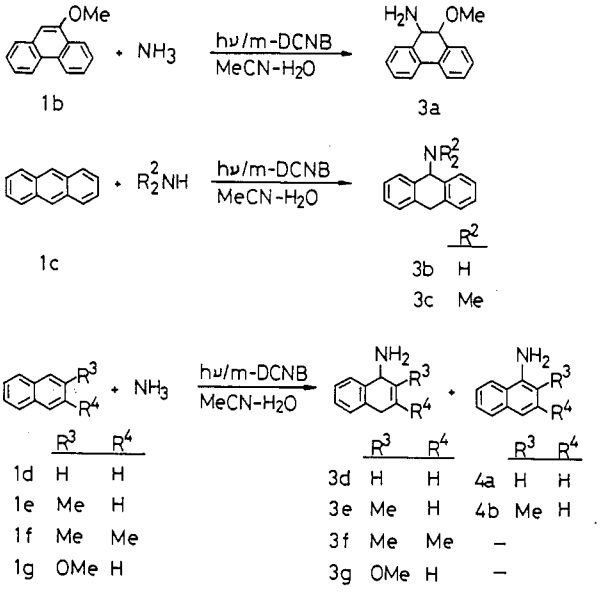
run	arenes	A[b]	irradn time, h	products (yields, %)[c]	convn of 1, %	recov of A, %
1	9-methoxyphenanthrene (**1b**)	*m*-DCNB	2	**3a** (99)	95	83
2	anthracene (**1c**)	*m*-DCNB	18	**3b** (88)	82[d]	100
3	naphthalene (**1d**)	*m*-DCNB	20	**3d** (48), **4a** (13)	79	100
4	2-methylnaphthalene (**1e**)	*m*-DCNB	15	**3e** (36), **4b** (19)	76	87
5	2,3-dimethylnaphthalene (**1f**)	*m*-DCNB	10	**3f** (81)	81	99
6	2-methoxynaphthalene (**1g**)	*m*-DCNB	7	**3g** (75)	92	100
7	1-methylnaphthalene (**1h**)	*m*-DCNB	10	**3h** (15), **3i** (39), **3j** (23)	88	90
8	2-acetylnaphthalene ethylene glycol acetal (**1i**)	*m*-DCNB	12	**3k** (26), **3l** (24), **4c** (19)	74	98
9	1-methoxynaphthalene (**1j**)	*m*-DCNB	10	**3m** (19), **4a** (23), **5** (12), **6** (20)	63	93
10[e]	1-methoxynaphthalene (**1j**)		10	**4a** (21)	9	
11	1-chloronaphthalene (**1k**)	*m*-DCNB	7	**3n** (11), **4a** (24), **1d** (3)	38	97
12[e]	1-chloronaphthalene (**1k**)		7	**1d** (8)	11	
13	*m*-dimethoxybenzene (**1l**)	CNN	20	**4d** (41), **4e** (17)	31	51
14[f]	biphenyl (**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 solubility of **1c**. [b] Electron acceptors: *m*-DCNB = *m*-dicyanobenzene, CNN = 1-naphthonitrile, 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 the photodimer. [e] In the absence of *m*-DCNB. [f] Under oxygen atmosphere. [g] Not determined.

Chart I



Scheme III



DCNB was mostly recovered except in a few cases. For synthetic purposes, 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 II. 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-methoxynaphthalene (**1g**) to yield 1-amino-1,4-dihydronaphthalenes **3f** and **3g**, while both the corresponding 1-amino-1,4-dihydronaphthalenes (**3d** and **3e**) and 1-naphthylamines (**4a** and **4b**) were formed from naphthalene (**1d**) and 2-methylnaphthalene (**1e**) (Scheme III). On the other hand, photoamination of the other naphthalene derivatives gave mixtures of aminated products, which are shown in Chart I. The products were separated by column chromatography of their acetylated compounds on silica gel and were identified by extensive NMR analysis involving spin decoupling as well as lanthanoid-induced shifts.

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 the 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-methoxyaniline (**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

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

run	arenes	amines	irradn time, h	products[b] (yields, %)[c]	convn of 1, %	recov of m-DCNB, %
1	phenanthrene (1a)	Me_2NH	50	**2n** (40), **7a** (3), **9a** (25)	55	29
2[d]	phenanthrene (1a)	Me_2NH	50	**2n** (7), **7a** (15)	54	
3	phenanthrene (1a)	Et_2NH	50	**2o** (26), **7a** (6), **9b** (2)	31	49
4	anthracene (1c)	Me_2NH	2	**3c** (73), **7b** (11), 8 (4)	96	98
5[d]	anthracene (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] In the absence of *m*-DCNB.

2-aminobiphenyl (**4f** and **4g**) in the presence of DCNA.

Photoamination with Secondary Amines. Table III 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** or **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,[8] 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.

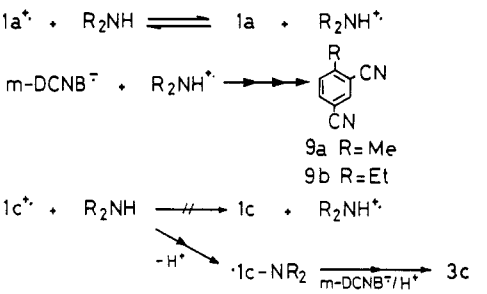
Discussion

The photoamination reaction has thus been shown to be applicable to the efficient, direct amination of various arenes using ammonia and unactivated 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 allylamine 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.

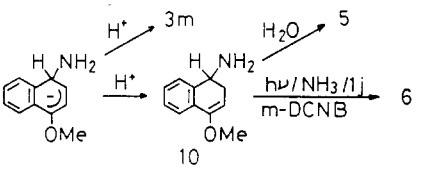
As has been discussed earlier,[4] this facile photoamination is initiated by photochemical electron transfer from the arenes to the electron acceptor[3a-c,9] followed by nucleophilic attack of ammonia or primary amines on the aromatic cation radicals (Scheme I). The one-electron reduction of the aminated neutral radicals by the anion radical of the electron acceptor gives 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 both the 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 hand, the photoaddition of ammonia to **1i** shows that steric effects should also be taken into account.

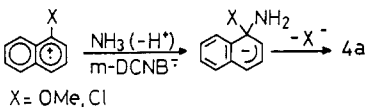
The formation of **5** and **6** from the photoreaction of **1j** probably arises from hydrolysis and further photoamination, respectively, of an intermediate product **10**.

Scheme IV



Since **10** is a very electron-rich olefin, the cation radical of **1j** might efficiently undergo electron exchange with **10**[3c] to generate the cation radical of **10**, which is reacted 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.





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 IV).[10]

Experimental Section

Melting points were determined with a Yanagimoto hot stage and are uncorrected. ^1H NMR spectra were measured on a JEOL JNM-60 spectrometer at 60 MHz or on a Bruker AM-360 spectrometer at 360 MHz with tetramethylsilane as internal standard. IR spectra were taken on a Hitachi 260-50 spectrometer and mass spectra on a JEOL JMS-D300S equipped with data analyzer JEC-980B. GLC analyses were carried out on a Shimadzu GC-8A or a Hitachi 163 with flame-ionization detectors using a 50 cm × 4 mm column of 2% silicone OV-17, 2% silicone OV-1, or 25% silicone DC-550 on Chromosorb WAW DMCS.

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(9) Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265–5373.
(10) Details of the mechanism will be published elsewhere.

Spectral grade acetonitrile was used without further purification. All the arenes, *m*-dicyanobenzene, 1-naphthonitrile, 9,10-dicyanoanthracene, and the amines were commercially available (Tokyo Kasei and Nakarai Chemicals) and purified by recrystallization or distillation as usual.

Photoamination of Arenes. General Procedures. 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 the solution was bubbled with argon for 20 min. In the case of such volatile amines as methylamine and ethylamine, each aqueous solution of the amines was added to a solution of an arene and an electron acceptor after argon bubbling, whereas ammonia solutions were obtained by dissolving gaseous ammonia into argon-bubbled 9:1 (v/v) acetonitrile–water solutions 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 solutions 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 solutions. 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 time, yields of the products, recovered yields of the electron acceptor, and conversions of the arenes are listed in Tables I–III.

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

***N*-Methyl-9-amino-9,10-dihydrophenanthrene (2b)**: ^1H NMR (CCl_4) δ 1.2 (br s, 1 H), 2.23 (s, 3 H), 2.92–3.00 (m, 2 H), 3.5 (t, J = 5 Hz, 1 H), 7.0–7.18 (m, 6 H), 7.5–7.7 (m, 2 H); IR ($CHCl_3$) 3310 cm^{-1}. The acetamide: mp 121–122 °C (from methanol); MS (CI method), *m/e* 252 ($M^+ + 1$), 178 ($M^+ - NH_2COMe$). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; H, 5.57. Found: C, 81.39; H, 6.80; N, 5.62.

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

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

***N*-*tert*-Butyl-9-amino-9,10-dihydrophenanthrene (2e)**: mp 73–74 °C (from methanol); ^1H NMR (CCl_4) δ 0.83 (br s, 1 H), 1.13 (s, 9 H), 2.73–2.89 (m, 2 H), 3.76–3.96 (dd, J = 5, 8 Hz, 1 H), 7.0–7.23 (m, 6 H), 7.33–7.66 (m, 2 H); IR ($CHCl_3$) 3310 cm^{-1}; MS, *m/e* 251 (M^+), 263 ($M^+ - CH_3$), 194 ($M^+ - C_4H_9$), 178 ($M^+ - C_4H_9NH_2$). Anal. Calcd for $C_{18}H_{21}N$: C, 86.01; H, 8.42; N, 5.77. Found: C, 85.77; H, 8.41; N, 5.44.

***N*-Benzyl-9-amino-9,10-dihydrophenanthrene (2f)**: ^1H NMR (CCl_4) δ 1.36 (br s, 1 H), 2.87–3.00 (m, 2 H), 3.50–3.70 (m, 3 H), 6.93–7.11 (m, 11 H), 7.4–7.6 (m, 2 H); IR ($CHCl_3$) 3310 cm^{-1}; MS, *m/e* 285 (M^+), 194 ($M^+ - CH_2Ph$), 178 ($M^+ - NH_2CH_2Ph$). The acetamide: mp 117–118 °C (from methanol). Anal. Calcd for $C_{27}H_{23}NO$: C, 84.37; H, 6.47; N, 4.28. Found: C, 84.19; H, 6.38; N, 4.21.

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

***N*-Allyl-9-amino-9,10-dihydrophenanthrene (2h)**: ^1H NMR (CCl_4) δ 1.36 (br s, 1 H), 2.8–3.1 (m, 4 H), 3.67 (t, J = 5 Hz, 1 H), 4.8–5.27 (m, 2 H), 5.4–5.9 (m, 1 H), 7.0–7.2 (m, 6 H), 7.5–7.7 (m, 2 H); IR (CCl_4) 3310 cm^{-1}; MS, *m/e* 235 (M^+), 194 ($M^+ - C_3H_5$), 178 ($M^+ - NH_2C_3H_5$). The acetamide: mp 130–131 °C (from methanol). Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.91; N, 5.05. Found: C, 82.03; H, 6.71; N, 5.03.

***N*-(2-Cyanoethyl)-9-amino-9,10-dihydrophenanthrene (2i)**: ^1H NMR (CCl_4) δ 1.2 (br s, 1 H), 2.07–2.26 (m, 2 H), 2.6–2.76 (m, 2 H), 2.86–3.03 (m, 2 H), 3.7 (t, J = 5 Hz, 1 H), 7.0–7.2 (m, 6 H), 7.5–7.7 (m, 2 H); IR ($CHCl_3$) 3310, 2250 cm^{-1}; MS, *m/e* 248 (M^+), 178 ($M^+ - C_3H_6N_2$). The acetamide: mp 151–152 °C (from methanol). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.48; H, 6.26; N, 9.65.

***N*-(2-Hydroxyethyl)-9-amino-9,10-dihydrophenanthrene (2j)**: mp 105–105.5 °C (from chloroform–ether); ^1H NMR (CCl_4) δ 2.10 (br s, 2 H), 2.41–2.64 (m, 2 H), 2.96–3.05 (m, 2 H), 3.25–3.43 (m, 2 H), 3.66 (t, J = 4 Hz, 1 H), 7.0–7.2 (m, 6 H), 7.5–7.7 (m, 2 H); IR ($CHCl_3$) 3400, 3310 cm^{-1}; MS, *m/e* 239 (M^+), 193 ($M^+ - C_2H_6O$), 178 ($M^+ - C_2H_7NO$). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 79.93; H, 7.08; N, 5.87.

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

***N*-(2-Acetamidoethyl)-9-amino-9,10-dihydrophenanthrene (2l)**: ^1H NMR (CCl_4) δ 1.4 (br s, 1 H), 1.64 (s, 3 H), 2.43–2.60 (m, 2 H), 2.79–2.96 (m, 4 H), 3.56 (t, J = 4 Hz, 1 H), 6.17 (br s, 1 H), 6.92–7.24 (m, 6 H), 7.36–7.56 (m, 2 H); IR ($CHCl_3$) 3440, 1670 cm^{-1}; MS, *m/e* 280 (M^+), 208 ($M^+ - C_3H_6NO$), 194 ($M^+ - C_4H_8NO$), 178 ($M^+ - C_4H_{10}N_2O$). The benzamide: mp 229–230 °C (from methanol). Anal. Calcd for $C_{25}H_{24}N_2O_2$: C, 78.10; H, 6.29; N, 7.29. Found: C, 77.79; H, 6.22; N, 7.13.

***N*-((Ethoxycarbonyl)methyl)-9-amino-9,10-dihydrophenanthrene (2m)**: ^1H NMR (CCl_4) δ 1.18 (t, J = 7 Hz, 3 H), 1.58 (br s, 1 H), 2.86–2.96 (m, 2 H), 3.17 (s, 2 H), 3.70 (t, J = 5 Hz, 1 H), 4.0 (q, J = 7 Hz, 2 H), 7.0–7.2 (m, 6 H), 7.5–7.7 (m, 2 H); IR ($CHCl_3$) 3320, 1720 cm^{-1}; MS, *m/e* 281 (M^+), 178 ($M^+ - C_4H_9NO_2$). The benzamide: 183–183.5 °C (from ethanol). Anal. Calcd for $C_{25}H_{23}NO_3$: C, 77.90; H, 6.01; N, 3.63. Found: C, 77.59; H, 5.96; N, 3.45.

***N*,*N*-Dimethyl-9-amino-9,10-dihydrophenanthrene (2n)**: ^1H NMR (CCl_4) δ 2.83 (s, 6 H), 2.73–2.89 (m, 2 H), 3.53 (t, J = 6 Hz, 1 H), 6.86–7.20 (m, 6 H), 7.26–7.53 (m, 2 H); MS, *m/e* 223 (M^+), 209 ($M^+ - CH_2$), 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 Eshweiler–Clarke.[11]

***N*,*N*-Diethyl-9-amino-9,10-dihydrophenanthrene (2o)**: ^1H NMR (CCl_4) δ 0.96 (t, J = 7 Hz, 6 H), 2.5 (q, J = 7 Hz, 4 H), 2.94–3.03 (m, 2 H), 3.69 (t, J = 4 Hz), 7.0–7.2 (m, 6 H), 7.46–7.73 (m, 2 H); MS, *m/e* 251 (M^+), 223 ($M^+ - 2 \times CH_3$), 194 ($M^+ - 2 \times Et$), 178 ($M^+ - NEt_2$). The dehydrogenation of **2o** by Pd–C gave *N*,*N*-diethyl-9-aminophenanthrene.[12]

9-Amino-10-methoxy-9,10-dihydrophenanthrene (3a): ^1H NMR ($CDCl_3$) δ 1.69 (br s, 2 H), 3.36 (s, 3 H), 4.12 (d, J = 4 Hz, 1 H), 4.23 (d, J = 4 Hz, 1 H), 7.1–7.4 (m, 6 H), 7.56–7.79 (m, 2 H); IR ($CHCl_3$) 3360, 3300 cm^{-1}; MS, *m/e* 225 (M^+), 210 ($M^+ - Me$), 193 ($M^+ - MeOH$), 178 ($M^+ - MeOH - NH_2$). The acetamide: mp 163–165 °C (from hexane–benzene). Anal. Calcd for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.14; H, 6.30; N, 5.18.

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9-Amino-9,10-dihydroanthracene (3b): ^{1}H NMR ($CDCl_3$) δ 1.6 (br s, 2 H), 3.7–4.1 (AB d, J = 18 Hz, 2 H), 4.7 (s, 1 H), 6.9–7.5 (m, 8 H); IR ($CHCl_3$) 3380, 3310 cm^{-1}. The acetamide: mp 206.5–207 °C (from benzene); MS (CI method), m/e 238 (M^+ + 1), 179 (M^+ + 1 – NHCOMe). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.10; H, 6.39; N, 5.95.

***N,N*-Dimethyl-9-amino-9,10-dihydroanthracene (3c)**: mp 67–69 °C (from benzene); ^{1}H NMR (CCl_4) δ 2.0 (s, 6 H), 3.4–4.33 (AB d, J = 16 Hz, 2 H), 4.07 (s, 1 H), 6.96–7.13 (m, 8 H); MS, m/e 223 (M^+), 208 (M^+ – Me), 193 (M^+ – 2 × Me), 178 (M^+ – $NHMe_2$). Compound **3c** was identified with an authentic sample prepared according to the reported method.[8]

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 156–157 °C (from hexane–benzene); ^{1}H NMR ($CDCl_3$, 360 MHz) δ 2.02 (s, 3 H), 3.32–3.49 (m, 2 H), 5.7 (br s, 1 H), 5.75–5.81 (m, 1 H), 5.86–5.92 (m, 1 H), 6.07–6.12 (m, 2 H), 7.13–7.17 (m, 1 H), 7.21–7.29 (m, 2 H), 7.38–7.43 (m, 1 H); IR ($CHCl_3$) 3440, 1680 cm^{-1}; MS, m/e 187 (M^+), 144 (M^+ – COMe), 128 (M^+ – NH_2COMe). Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.93; H, 6.97; N, 7.44. 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 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); ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.84 (s, 3 H), 2.00 (s, 3 H), 3.29–3.49 (m, 2 H), 5.58 (br s, 1 H), 5.67–5.73 (m, 1 H), 5.80–5.85 (m, 1 H), 7.12–7.15 (m, 1 H), 7.18–7.35 (m, 2 H), 7.38–7.43 (m, 1 H); IR ($CHCl_3$) 3340, 1660 cm^{-1}; MS, m/e 201 (M^+), 142 (M^+ – NH_2COMe), 140. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.29; H, 7.46; N, 6.91. 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); ^{1}H NMR ($CDCl_3$) δ 1.63 (s, 1 H), 1.68 and 2.35 (s, 3 H), 2.26 and 2.43 (s, 3 H), 7.18–7.86 (m, 6 H); IR ($CHCl_3$) 3440, 1680 cm^{-1}; MS, m/e 199 (M^+). Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.31; H, 6.56; N, 6.86. 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): ^{1}H NMR (CCl_4) δ 1.29 (br s, 2 H), 1.62 (s, 3 H), 1.72 (s, 3 H), 3.02 (br s, 2 H), 3.83 (br s, 1 H), 6.75–7.05 (m, 4 H); IR ($CHCl_3$) 3360, 3300 cm^{-1}. The acetamide: mp 201–202 °C (from methanol); ^{1}H NMR ($CDCl_3$) δ 1.76 (s, 6 H), 1.92 (s, 3 H), 3.28 (s, 2 H), 5.58 (br s, 2 H), 7.0–7.26 (m, 4 H); IR ($CHCl_3$) 3450, 1660 cm^{-1}; MS, m/e 215 (M^+), 172 (M^+ – COMe), 156 (M^+ – NH_2COMe). Anal. Calcd for $C_{14}H_{17}NO$: C, 78.10; H, 7.96; N, 6.51. Found: C, 78.13; H, 7.98; N, 6.53.

1-Amino-2-methoxy-1,4-dihydronaphthalene (3g): ^{1}H NMR (CCl_4) δ 2.59 (br s, 2 H), 2.33–2.46 (m, 2 H), 2.5 (s, 3 H), 4.13–4.33 (m, 1 H), 4.5–4.83 (m, 1 H), 6.92–7.10 (m, 3 H), 7.33–7.59 (m, 1 H); IR ($CHCl_3$) 3360, 3300 cm^{-1}. The acetamide: mp 186–187 °C (from methanol); ^{1}H NMR ($CDCl_3$) δ 1.98 (s, 3 H), 3.33–3.50 (m, 2 H), 3.53 (s, 3 H), 4.92 (t, J = 4 Hz, 1 H), 5.69 (br s, 2 H), 7.0–7.2 (m, 4 H); IR ($CHCl_3$) 3470, 1670 cm^{-1}; MS, m/e 217 (M^+), 174 (M^+ – COMe), 158 (M^+ – NH_2COMe). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.87; H, 7.00; N, 6.46.

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 (d, J = 8 Hz, 3 H), 1.9 (s, 3 H), 3.1–3.6 (m, 1 H), 5.4–6.2 (m, 4 H), 7.0–7.3 (m, 4 H); IR ($CHCl_3$) 3430, 1660 cm^{-1}; MS, m/e 201 (M^+), 186 (M^+ – Me), 158 (M^+ – COMe), 142 (M^+ – NH_2COMe), 128. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.40; H, 7.37; N, 6.84. The acetamide of **3i**: mp 190–192 °C (from hexane–benzene); ^{1}H NMR ($CDCl_3$) δ 1.9 (s, 3 H), 2.1–2.2 (m, 3 H), 2.4–2.7 (m, 2 H), 5.0–5.4 (m, 1 H), 5.6–6.1 (m, 2 H), 7.1–7.4 (m, 4 H); IR ($CHCl_3$) 3440, 1660 cm^{-1}; MS, m/e 201 (M^+), 186 (M^+ – Me), 158 (M^+ – COMe), 142 (M^+ – NH_2COMe), 128. Anal. Calcd for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.48; H, 7.21; N, 6.96. The acetamide of **3j**: ^{1}H NMR ($CDCl_3$) δ 1.6 (s, 3 H), 1.9 (s, 3 H), 3.35 (br s, 2 H), 5.7–6.1 (m, 3 H), 7.0–7.4 (m, 4 H); IR ($CHCl_3$) 3450, 1670 cm^{-1}; MS, m/e 201 (M^+), 186 (M^+ – Me), 158 (M^+ – COMe), 142 (M^+ – NH_2COMe), 128. Compound **3j** was crystallized as the benzamide: mp 191–193 °C (from hexane–benzene); ^{1}H NMR ($CDCl_3$) δ 1.73 (s, 3 H), 3.46 (br s, 2 H), 5.96–6.07 (m, 2 H), 6.5 (br s, 1 H), 7.06–7.76 (m, 9 H). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.63; H, 6.39; N, 5.18.

Photoamination of 2-Acetylnaphthalene 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-acetylnaphthalene and *m*-DCNB. Further elution with benzene–ethyl acetate gave *N*-acetyl-5-amino-2-acetyl-5,8-dihydronaphthalene, *N*-acetyl-8-amino-2-acetylnaphthalene, and *N*-acetyl-8-amino-2-acetyl-5,8-dihydronaphthalene. *N*-Acetyl-8-amino-2-acetyl-5,8-dihydronaphthalene: mp 163–164 °C (from hexane–ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 2.5 (s, 3 H), 3.3–3.5 (m, 2 H), 5.6–6.0 (m, 4 H), 7.1 (d, J = 8 Hz, 1 H), 7.6 (d, J = 8 Hz, 1 H), 7.8 (br s, 1 H); IR ($CHCl_3$) 3430, 1680, 1660 cm^{-1}; MS, m/e 229 (M^+), 186 (M^+ – COMe), 170 (M^+ – NH_2COMe), 155, 143, 127. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 72.92; H, 6.54; N, 6.01. *N*-Acetyl-5-amino-2-acetyl-5,8-dihydronaphthalene: mp 159–160 °C (from hexane–ethyl acetate); ^{1}H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 2.5 (s, 3 H), 3.3–3.5 (m, 2 H), 5.6–6.2 (m, 4 H), 7.4 (d, J = 8 Hz, 1 H), 7.6 (br s, 1 H), 7.6 (d, J = 8 Hz, 1 H); IR ($CHCl_3$) 3440, 1690, 1665 cm^{-1}; MS, m/e 229 (M^+), 186 (M^+ – COMe), 170 (M^+ – NH_2COMe), 155, 144, 127. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11. Found: C, 73.00; H, 6.51; N, 6.02. *N*-Acetyl-8-amino-2-acetylnaphthalene: mp 199–200 °C (from hexane–ethyl acetate); ^{1}H NMR (CD_3CO-CD_3) δ 1.6 (br s, 1 H), 2.2 (s, 3 H), 2.6 (s, 3 H), 7.4–7.6 (m, 2 H), 7.8–8.1 (m, 3 H), 8.2 (br s, 1 H); IR (KBr) 3440, 1680, 1665 cm^{-1}; MS, m/e 227 (M^+), 185 (M^+ – $COCH_2$), 170 (M^+ – NCOMe), 142, 115. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77; N, 6.16. Found: C, 73.70; H, 5.65; N, 6.09.

The Photoamination of 1-Methoxynaphthalene (1j) with Ammonia. After the solution was evaporated from the irradiated solutions, the residue was acetylated with Ac_2O–pyridine. 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 (s, 3 H), 3.1 (s, 3 H), 5.0–5.1 (m, 1 H), 5.6–5.8 (m, 2 H), 6.1–6.2 (m, 2 H), 7.3–7.6 (m, 4 H); IR ($CHCl_3$) 3340, 1660 cm^{-1}; MS, m/e 186 (M^+ – OMe), 184, 158 (M^+ – H_2COMe), 142 (M^+ – HOMe – COMe). Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.82; H, 6.91; N, 6.59. The acetamide of **5**: mp 145–146 °C (from hexane–benzene); ^{1}H NMR ($CDCl_3$) δ 2.1 (s, 3 H), 2.2–2.4 (m, 2 H), 2.6–2.8 (m, 2 H), 5.1–5.5 (m, 1 H), 5.7–6.1 (m, 1 H), 7.3–7.5 (m, 3 H), 7.8–8.0 (m, 1 H); IR ($CHCl_3$) 3440, 1690, 1665 cm^{-1}; MS, m/e 203 (M^+), 160 (M^+ – COMe), 144 (M^+ – NH_2COMe), 133. Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.91; H, 6.45; N, 6.89. Found: C, 70.84; H, 6.45; N, 6.88. The diacetamide of **6**: mp 274–275 °C (from ethyl acetate–ethanol); ^{1}H NMR ($CDCl_3$, 360 MHz) δ 1.78–1.85 (m, 1 H), 1.96 (s, 3 H), 2.06 (s, 3 H), 2.68–2.95 (m, 1 H), 3.30 (s, 3 H), 4.33–4.40 (m, 1 H), 4.53 (d, J = 6.9 Hz, 1 H), 5.05 (dd, J = 7.3, 5.3 Hz, 1 H), 6.21 (br s, 1 H), 6.50 (br s, 1 H), 7.28–7.37 (m, 4 H); IR (KBr) 3280, 1645 cm^{-1}; MS, m/e 276 (M^+), 245, (M^+ – OMe), 217 (M^+ – H_2NCOMe), 201, 191, 185, 158, 147, 143, 134, 117. Anal. Calcd for $C_{15}H_{20}N_2O_3$: C, 65.19; H, 7.30; N, 10.14. Found: C, 65.18; H, 7.18; N, 9.99.

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); ^{1}H NMR ($CDCl_3$) δ 1.9 (s, 3 H), 3.4–3.5 (m, 2 H), 5.4–5.8 (m, 2 H), 5.9–6.0 (m, 2 H), 7.0–7.3 (m, 3 H); IR ($CHCl_3$) 3340, 1670 cm^{-1}; MS, *m/e* 221 (M^+), 186 (M^+ – Cl), 162 (M^+ – NH_2COMe), 143, 128. Anal. Calcd for $C_{12}H_{12}NOCl$: C, 65.01; H, 5.46; N, 6.32; Cl, 15.99. Found: C, 64.92; H, 5.44; N, 6.33; Cl, 15.69.

Photoamination of *m*-Dimethoxybenzene (1l). The aminated products were acetylated 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); ^{1}H NMR ($CDCl_3$) δ 2.15 (s, 3 H), 3.75 (s, 3 H), 3.80 (s, 3 H), 6.25–6.6 (m, 2 H), 7.55 (br s, 1 H), 8.0–8.3 (m, 1 H); IR ($CHCl_3$) 3450, 1680 cm^{-1}; MS, *m/e* 195 (M^+), 137 (M^+ – NHCOMe). Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.52; H, 6.71; N, 7.18. Found: C, 61.43; H, 7.00; N, 7.13. The acetamide of **4e**: ^{1}H NMR (CCl_4) δ 2.05 (s, 3 H), 3.75 (s, 3 H), 6.5–7.0 (m, 3 H), 7.65 (br s, 1 H), 8.1–8.4 (m, 1 H). 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 authentic samples. Compound **4f**: mp 176–177 °C (for the acetamide; from benzene); ^{1}H NMR (CCl_4) δ 3.40 (br s, 2 H), 6.25–6.70 (m, 2 H), 6.9–7.7 (m, 7 H); IR 3480, 3400 cm^{-1}. Compound **4g**: ^{1}H NMR (CCl_4) δ 3.56 (br s, 2 H), 6.4–7.5 (m, 9 H); IR ($CHCl_3$) 3480, 3400 cm^{-1}.

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

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

BF_3-Catalyzed Cycloadditions of Naturally Occurring Sesquiterpene *p*-Benzoquinones

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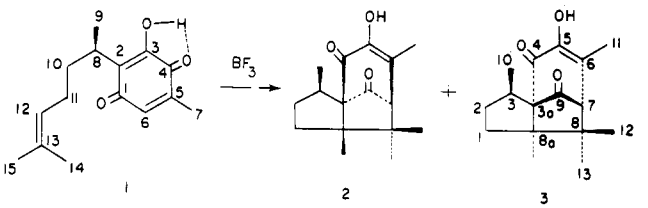
Lewis acid catalyzed reactions of all known naturally occurring perezone analogues and two allylic alcohols prepared from perezone and hydroxyperezone show that these *p*-benzoquinones exhibit a complex behavior upon acid treatment. As in the case of perezone, *O*-angeloylperezone and 6-angeloxyperezone afforded pipitzol analogues. Hydroxyperezone and *O*-angeloyl-6-hydroxyperezone yielded a stable boron adduct of perezinone. Curcuquinone, the simplest sesquiterpene quinone, afforded mainly polymeric material, while 15-hydroxyperezone and hydroxyperezone derivatives gave a dibenzofurandione and a tricyclic molecule containing a new skeleton, respectively. The results for *O*-angeloylperezone, compared with those of perezone, show that steric effects play an important role in these transformation allowing at present complete stereocontrol of the reaction outcome.

Cycloaddition reactions have been a subject of increased interest and continue to attract attention largely due to their synthetic versatility.[1-4] However, little attention has been paid to intramolecular cycloadditions of the type represented by the perezone (**1**) to pipitzol (**2** and **3**) transformation.[5] Previous investigations of the thermally allowed reaction of perezone (**1**) have shown that it involves the coexistence of a sigmatropic change of order [1, 9] and a type B, ionic [$_\pi4_s + _\pi2_s$] cycloaddition.[6,7] Classically, the thermal transformation has been performed by refluxing perezone (**1**) in tetralin[8,9] or cumene,[10] affording an equimolecular mixture of α- (**2**) and β-pipitzol (**3**). Later, it



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was revealed that perezone (**1**) undergoes a mild highly stereoselective cycloaddition in the presence of boron trifluoride etherate to yield a 9:1 mixture of α- (**1**) and β-pipitzol (**2**) in 98% yield.[11] Subsequent studies also demonstrated that the stereoselectivity may be reversed in favor of the β isomer (**3**) by $AlCl_3$–Et_2S treatment of *O*-methylperezone, presumably due to steric crowding between the secondary methyl and methoxyl groups in the transition state.[12] The data provided so far seem to in-

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