Photochemical Alkylamination of 1-Acylaminoanthraquinones

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The photochemical reaction of 1-acylaminoanthraquinones(1) with primary aliphatic amines in benzene, in air, gave 1-acylamino-4-alkylaminoanthraquinones (2) in 56—78% yields. The reaction was retarded by the addition of triplet quenchers. The quantum yield of the reaction increased on raising the amine concentration. A mechanism *via* addition of alkylamine to the triplet excited state of (1), followed by oxidation to give the products (2), is proposed. The regioselective 4-amination of (1) has been rationalized by means of the frontier orbital method.

Recently the photochemical substitution of anthraquinone derivatives has attracted considerable attention. Many reports have been written on the replacement of sulpho,[1,2] methoxy,[3,4] nitro,[5] and halogeno [6,7] groups by amines or other nucleophiles. Even substitution of the hydrogen atoms of the anthraquinone nucleus by amines has been found to occur for sulpho-[1c] and methoxy-anthraquinones[3] and anthraquinone itself.[8,9] The mechanism of these photochemical substitutions is complex and is sensitive to the nucleophile, the solvent, and the multiplicity of the excited state of the substrate. We have also recently found that 1-benzoylaminoanthraquinone (1a) undergoes direct photoamination in the presence of primary aliphatic amines to give the 1-benzoylamino-4-alkylaminoanthraquinones (2a—f).[10]
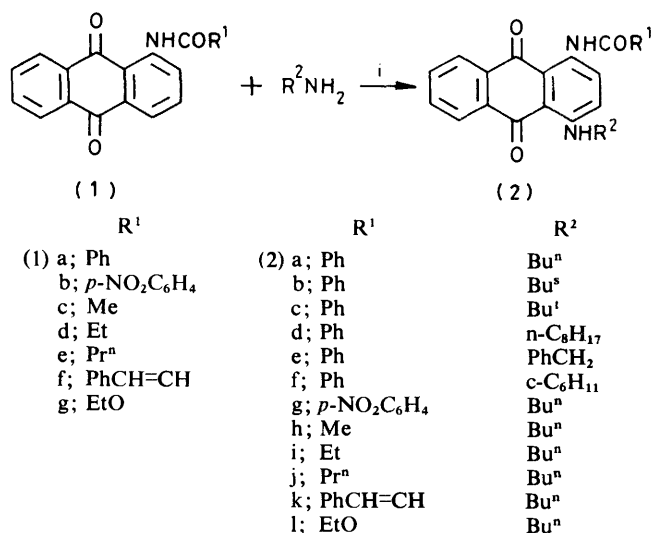
In this paper we report the details of the direct photoamination of the 1-acylaminoanthraquinones (1) with alkylamines and propose a possible mechanism for the reaction.

Results and Discussion

When an aerated benzene solution of the anthraquinone (1) (7.5 × 10⁻⁴ mol/l) and alkylamine (0.3 mol/l) was irradiated with a Pyrex-filtered high-pressure mercury lamp, the colour of the solution turned from the initial pale yellow to deep purplish-blue.

As an example, the change in the visible spectra of a benzene solution of the benzoylaminoanthraquinone (1a) with butylamine is shown in Figure 1. The absorbance at *ca.* 420 nm, characteristic of (1a), disappeared during the irradiation and new double headed peaks, characteristic of 1,4-bis(substituted amino)anthraquinones (2), appeared at *ca.* 568 and *ca.* 606 nm, and isosbestic points were observed at 380 and 471 nm.

T.l.c. analysis (silica gel, benzene) showed that trace amounts of by-products were produced together with the main product, 1-benzoylamino-4-butylaminoanthraquinone (2a). The reactions of the quinone (1a) with other primary aliphatic amines, such as s-butylamine, t-butylamine, n-octylamine, benzylamine, and cyclohexylamine proceeded similarly, and the results are summarized in Table 1. The reaction proceeded smoothly in air or under oxygen (runs 1 and 2), but was suppressed considerably under nitrogen (run 3). Oxygen accelerates the direct photoamination and these observations have also been reported in the direct photoamination of methoxyanthraquinones[3b] and nitrophenazines.[11] The effect of oxygen as oxidant is shown in the Scheme. The rate of the amination was greatly influenced by the steric hindrance of the alkyl residue of the amine (compare the results of runs 1, 4, and 5). Secondary amines such as diethylamine, piperidine, and morpholine did not show a

	R¹		R¹	R²
(1)	a; Ph	(2)	a; Ph	Buⁿ
	b; *p*-NO₂C₆H₄		b; Ph	Buˢ
	c; Me		c; Ph	Buᵗ
	d; Et		d; Ph	n-C₈H₁₇
	e; Prⁿ		e; Ph	PhCH₂
	f; PhCH=CH		f; Ph	c-C₆H₁₁
	g; EtO		g; *p*-NO₂C₆H₄	Buⁿ
			h; Me	Buⁿ
			i; Et	Buⁿ
			j; Prⁿ	Buⁿ
			k; PhCH=CH	Buⁿ
			l; EtO	Buⁿ

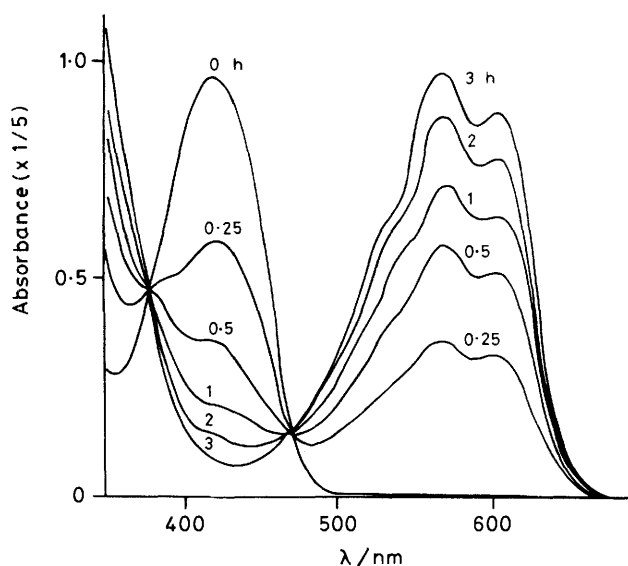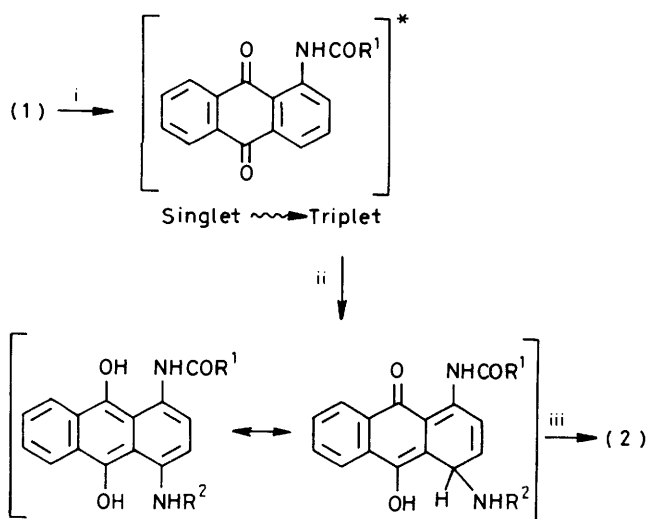*Reagents:* i, *hv* (≥300 nm), air

Figure 1. Changes in the visible spectrum on the photoamination of 1-benzoylaminoanthraquinone (1a) with n-butylamine in benzene at 30 °C (in air): [(1a)] = 7.5 × 10⁻⁴ mol/l, [butylamine] = 3.0 × 10⁻¹ mol/l

Scheme. Reagents: i, hv; ii, R^2NH_2; iii, oxidation by oxygen and/or (1)

Table 1. Photoamination of the benzoylaminoanthraquinone (1a) with alkylamines in benzene at 30 °C,[a] in air unless stated otherwise

Run	Amine	Time (h)	Aminated product	Yield (%)[c]
1	Bu^nNH_2	3.5[b]	(2a)	61
2	Bu^nNH_2[d]	3.5[b]	(2a)	64
3	Bu^nNH_2[e]	3.5	(2a)	11
4	Bu^sNH_2	5.5[b]	(2b)	61
5	Bu^tNH_2	8.0[b]	(2c)	56
6	$n-C_8H_{17}NH_2$	3.5[b]	(2d)	64
7	$PhCH_2NH_2$	3.5[b]	(2e)	58
8	$c-C_6H_{11}NH_2$	7.0[b]	(2f)	58

[a] [(1a)] = 7.5×10^{-4} mol/l, [alkylamine] = 3.0×10^{-1} mol/l, $\lambda \geqslant$ 300 nm. [b] Irradiation time for the maximum yield of (2). [c] Determined by spectrophotometry. [d] Under oxygen. [e] Under nitrogen.

similar direct photoamination, and in these cases photodegradation of (1a) took place. The possibility of photoamination with aniline and p-anisidine was also investigated; however, photodegradation analogous to that occurring with the secondary alkylamines was observed.

The effects of the solvent on the photoamination of compound (1a) with n-butylamine are shown in Figure 2. The yields of the product amine (2a) were greatly dependent on the solvent. Benzene was the most suitable solvent and gave 4-aminated product (2a) regioselectively. When other solvents such as acetonitrile, pyridine, and chloroform were used, byproducts were also obtained and consequently the yield of (2a) was reduced. In the case of dioxane, the photodegradation of (1a) was the major reaction.

The irradiation wavelength also influences the reaction. Irradiation of a benzene solution of (1a) and n-butylamine with u.v. light ($\lambda < 300$ nm) resulted only in the photodegradation of (1a). Direct photoamination was found to occur on irradiation with light corresponding to the first absorption band of (1a) (λ 420 nm). The quantum yield from the photoamination was ca. 6×10^{-4} {[n-butylamine]/[(1a)] = 400} and increased with the amine concentration. A good linear relation was found between the reciprocals of the quantum yield and the amine concentration, as shown in Figure 3. This result suggests that a collision between the amine and an excited intermediate of (1a) is one of the steps on the photoamination pathway.

To investigate the reactive state of (1), quenching experiments were conducted. The presence of anthracene and trans-stilbene was found to reduce the quantum yield of the photoamination. Stern–Volmer plots gave straight lines as shown in Figure 4. The energies of the lowest excited singlet (S_1) and triplet (T_1) states for these compounds are as follows:[12] anthracene ($E_{S1} = 319$ and $E_{T1} = 176$ kJ/mol); trans-stilbene ($E_{S1} = 394$ and $E_{T1} = 209$ kJ/mol). The ^1CT state energy of (1a) has been estimated to be ca. 285 kJ/mol from the first absorption band at 420 nm. The energies of the triplet states of (1a) are considered to be $E_{T2}(^3n\pi^*) = ca.$ 251 kJ/mol, and the $T_1(^3CT)$ level lies lower than the $T_2(^3n\pi^*)$ level[6e] (see Figure 5). Therefore, the observed quenching effects have been interpreted in terms of the triplet–triplet energy transfer. These results indicate that the photoamination proceeds via the triplet state of (1a).

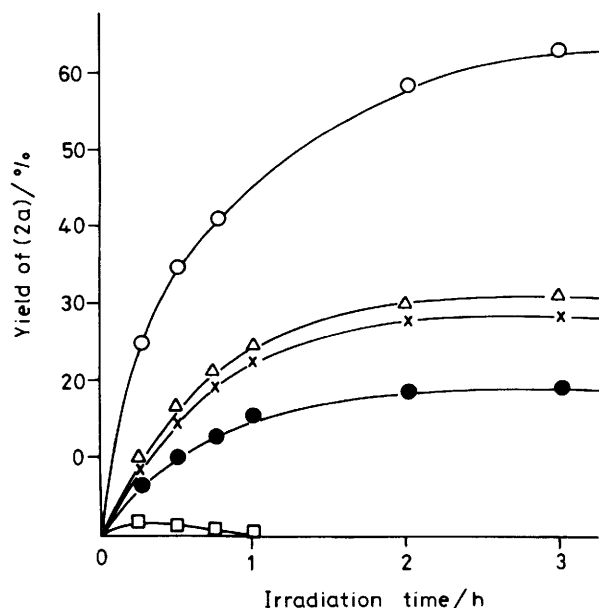As 1-aminoanthraquinone does not react under these

Figure 2. Solvent effect on the yield of the 1-benzoylamino-4-butylaminoanthraquinone (2a): [(1a)] = 7.5×10^{-4} mol/l, [butylamine] = 3.0×10^{-1} mol/l. Solvent: ○ benzene, △ pyridine, ● chloroform, × benzene–acetonitrile (v/v 1 : 1), and □ dioxane

conditions, its N-acylated derivatives were used for the photoamination. Various 1-acylaminoanthraquinones readily underwent direct photo-butylamination to give the corresponding products (2) in 58—78% yields (Table 2, run 1 and 9—13). The effect of varying the acyl group on the yields of compounds (2) was small. The presence of an ethoxyamido substituent ($NHCO_2Et$) also enhanced this photoamination (run 14). We have also found that 2-acylaminoanthraquinones and 1,2-(or 1,5-)bis(acylamino)anthraquinones undergo a similar direct photoamination. An investigation of the behaviour of these compounds will be reported elsewhere.

Inoue and Hida[13] have reported that the excited states of anthraquinones having an electron-donating substituent can be divided into two types, which are shown in the energy diagrams in Figure 5. In anthraquinones with strong donor substituents, the ^1CT level has a lower energy than the $^3n\pi^*$ level (Figure 5b), whereas, in those with weak donor substituents, the ^1CT level is at a higher energy than the $^3n\pi^*$
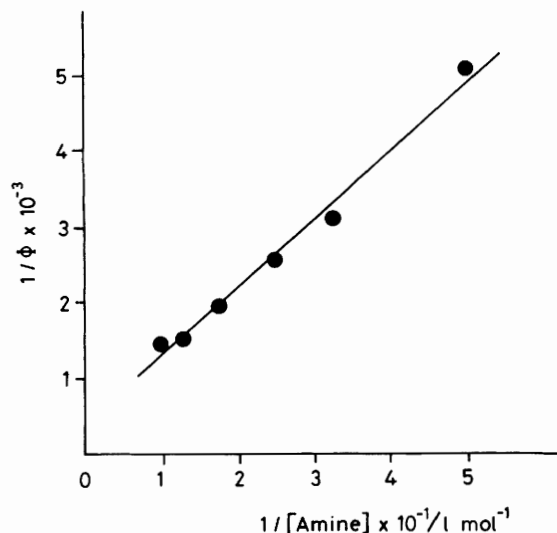
Figure 3. Effect of the concentration of amine on the quantum yield (Φ) from the photoamination of 1-benzoylaminoanthraquinone (1a): [(1a)] = 1.5×10^{-4} mol/l in benzene; irradiated with monochromatic light, λ 435.8 nm, in air

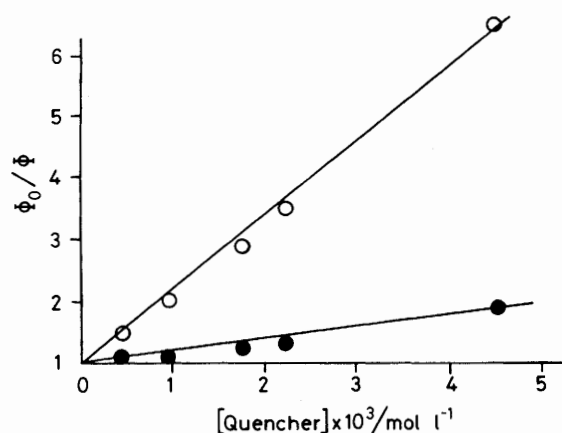**Figure 4.** Stern–Volmer plots for the photoamination of 1-benzoylaminoanthraquinone (1a) with butylamine: [(1a)] = 1.5×10^{-4} mol/l, [butylamine] = 6.0×10^{-2} mol/l; irradiated with monochromatic light, λ 435.8 nm, in air. ○ Anthracene, ● *trans*-stilbene

Table 2. Photoamination of acylaminoanthraquinones with n-butylamine in benzene in air at 30 °C [a]

Run	Substrate	Time [b] (h)	Aminated product	Yield (%) [c]
1	(1a)	3.5	(2a)	61
9	(1b)	3.5	(2g)	58
10	(1c)	3.0	(2h)	71
11	(1d)	3.0	(2i)	77
12	(1e)	3.0	(2j)	78
13	(1f)	5.5	(2k)	60
14	(1g)	3.0	(2l)	60

[a] [(1)] = 7.5×10^{-4} mol/l, [n-butylamine] = 3.0×10^{-1} mol/l, $\lambda \geqslant 300$ nm. 1-Aminoanthraquinone did not undergo photoamination under these conditions. [b] Irradiation times for the maximum yield of (2). [c] Determined by spectrophotometry.
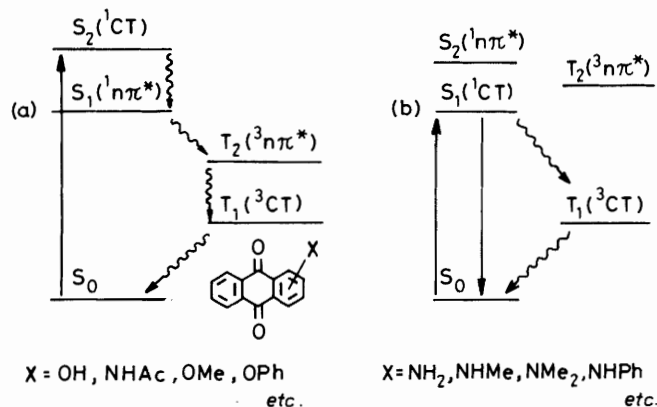

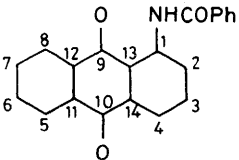**Figure 5.** Energy diagrams of the excited states of substituted anthraquinones (see ref. 13)

level (Figure 5a). Acylation of the amino group of aminoanthraquinones would therefore change the energy diagram from that shown in Figure 5b to that in 5a. Consequently, the intersystem crossing process $^1CT \longrightarrow {}^3n\pi^* \longrightarrow {}^3CT$ would be enhanced enabling direct photoamination *via* a triplet state to take place. The quenching experiments also support the proposal that the reaction proceeds *via* a triplet state of (1a); however, (1) has two triplet states, $T_2(^3n\pi^*)$ and $T_1(^3CT)$, and we could not determine which of them is the reactive state in the photoamination.

We were interested by the regioselective 4-alkylamination of (1). It is known that the orientation in photochemical aromatic substitutions is dependent on both the reaction mechanism and the frontier orbital electron densities of the substrate.[14–16] For example, in the photochemical nucleophilic substitution of an aromatic substrate, the S_N2Ar^* mechanism gives substitution at the positions which have high electron

densities in the HOMO † (HOMO-controlled reaction), whereas the S_N(ETANR ††)Ar* mechanism gives substitution at the positions which have high electron densities in the LUMO ††† (LUMO-controlled).[16] We therefore calculated the π-electron densities for the HOMO and LUMO of (1) as a basis for discussion of the orientation and the mechanism of the direct photoamination.

π-Electron densities for the HOMO and LUMO of (1a) were calculated by means of the Pariser–Parr–Pople (PPP) method [17] with a variable β,γ-approximation.[18] The results (Table 3) suggest that photoamination is likely to occur at the 4-position which has the highest electron density in the HOMO (HOMO-controlled).

Similar calculations were also carried out successfully for nitrophenazines, which were thought to undergo direct photoamination by the same mechanism.[11]

From the results described above a mechanism can be proposed for the direct photoamination of (1), as outlined in the Scheme. It is thought to proceed *via* the addition of primary alkylamines to a triplet state of (1). The regioselectivity at the 4-position is controlled by the electron density of the HOMO of (1). The resulting leuco-compound would be oxidized by atmospheric oxygen and/or the substrate (1) to give the 4-alkylaminated product (2).

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† Highest occupied molecular orbital. †† Electron transfer and addition of the nucleophile radical. ††† Lowest unoccupied molecular orbital.

Table 3. Calculated π-electron densities for the HOMO and LUMO of the benzoylaminoanthraquinone (1a)

	HOMO	LUMO
C(1)	0.173	0.045
C(2)	0.207	0.084
C(3)	0.025	0.102
C(4)	0.322 [a]	0.035
C(5)	0.004	0.032
C(6)	0.004	0.082
C(7)	0.000	0.074
C(8)	0.007	0.040
C(9)	0.006	0.271
C(10)	0.001	0.236
C(11)	0.000	0.112
C(12)	0.003	0.107
C(13)	0.234	0.109
C(14)	0.052	0.130

[a] Observed reaction site.

Experimental

All the m.p.s are uncorrected. The u.v.–vis and mass spectra were obtained with a Hitachi 220A spectrophotometer and a Hitachi RMU-6E mass spectrometer, respectively. The ^{1}H n.m.r. spectra were obtained with a Hitachi R-600 spectrometer using tetramethylsilane as internal standard. The elemental analyses were recorded on a Yanaco CHN recorder MT-2.

Materials.—1-Acylaminoanthraquinones (1a—g) were prepared by the acylation of 1-aminoanthraquinone with the corresponding acid chlorides [ethyl chlorocarbonate was used for the preparation of (1g)] and purified by column chromatography and/or recrystallization. Their structures were confirmed from the data shown below. All the other compounds and solvents were commercially available and were purified before use by the ordinary methods: 1-benzoylaminoanthraquinone (1a), m.p. 254—255 °C (lit.,[19] 254 °C) (Found: C, 77.25; H, 4.0; N, 4.2. Calc. for $C_{21}H_{13}NO_3$: C, 77.05; H, 4.00; N, 4.28%); $\lambda_{max.}$(benzene) 420 nm (ε 6 300).

1-(*p*-Nitrobenzoylamino)anthraquinone (1b), m.p. 273.5—274 °C (lit.,[19] 274 °C) (Found: C, 67.7; H, 3.0; N, 7.2. Calc. for $C_{21}H_{12}N_2O_5$: C, 67.74; H, 3.25; N, 7.52%); $\lambda_{max.}$(benzene) 416 nm (ε 6 600).

1-Acetylaminoanthraquinone (1c), m.p. 220—221 °C (lit.,[20] 219—220 °C) (Found: C, 72.3; H, 3.8; N, 5.1. Calc. for $C_{16}H_{11}NO_3$: C, 72.45; H, 4.18; N, 5.28%); $\lambda_{max.}$(benzene) 417 nm (ε 6 000).

1-Propionylaminoanthraquinone (1d), m.p. 176—176.5 °C (Found: C, 73.4; H, 4.6; N, 5.3%; M^+, 279. $C_{17}H_{13}NO_3$ requires C, 73.11; H, 4.69; N, 5.01%; *M*, 279); $\lambda_{max.}$(benzene) 418 nm (ε 6 100).

1-*Butyrylaminoanthraquinone* (1e), m.p. 162.5—163 °C (Found: C, 73.3; H, 4.95; N, 4.5%; M^+ 293. $C_{18}H_{15}NO_3$ requires C, 73.71; H, 5.15; N, 4.78%; *M*, 293); $\lambda_{max.}$(benzene) 419 nm (ε 6 200).

1-*Cinnamoylaminoanthraquinone* (1f), m.p. 223.5—224.5 °C

(Found: C, 78.1; H, 4.25; N, 4.1%; M^+, 353. $C_{23}H_{15}NO_3$ requires C, 78.18; H, 4.28; N, 3.96%; *M*, 353); $\lambda_{max.}$(benzene) 424 nm (ε 6 800).

1-Ethoxycarbonylaminoanthraquinone (1g), m.p. 214—215 °C (lit.,[21] 215 °C) (Found: C, 69.2; H, 4.3; N, 5.2. Calc. for $C_{17}H_{13}NO_4$: C, 69.15; H, 4.44; N, 5.40%); $\lambda_{max.}$(benzene) 417 nm (ε 5 900).

Photoamination of Compounds (1) *with Amines. General Procedure.*—A solution of (1) (7.5×10^{-4} mol/l) and a large excess of the amine (0.3 mol/l) was irradiated in air at 30 °C using a 400-W high-pressure mercury lamp equipped with a Pyrex cooling jacket. All the photoreactions were monitored by the visible spectra and t.l.c. Irradiation was continued until a maximum accumulation of the aminated product was obtained. After the reaction, the solvent was removed under reduced pressure, and then the residue was chromatographed on a silica-gel (Wakogel C-200) column with benzene as the eluant. The aminated products were purified by recrystallization from benzene and then identified. The properties of (2a) have already been described.[10] The isolated yields of the aminated products after the column chromatography were generally 70—95% of the values obtained by spectrophotometry (Tables 1 and 2).

1-*Benzoylamino-4-(s-butylamino)anthraquinone* (2b), m.p. 225.5—226 °C (Found: C, 75.2; H, 5.35; N, 6.7. $C_{25}H_{22}N_2O_3$ requires C, 75.36; H, 5.59; N, 7.03%); $\lambda_{max.}$(benzene) 572 (ε 11 400) and 610 nm (ε 10 000); δ_H (60 MHz; CDCl$_3$) 1.04 (3 H, t), 1.33 (3 H, d), 1.7 (2 H, m), 3.7 (1 H, m), 7.20 (1 H, d, *J* 10 Hz), 7.4—8.4 (9 H, m), 9.14 (1 H, d, *J* 10 Hz), 10.45 (1 H, br), and 13.52 (1 H, br).

1-*Benzoylamino-4-(t-butylamino)anthraquinone* (2c), m.p. 208—209 °C (Found: C, 75.3; H, 5.7; N, 6.9. $C_{25}H_{22}N_2O_3$ requires C, 75.36; H, 5.59; N, 7.03%); $\lambda_{max.}$(benzene) 573 (ε 10 800) and 612 nm (9 600); δ_H (CDCl$_3$) 1.60 (9 H, s), 7.34 (1 H, d, *J* 10 Hz), 7.4—8.4 (9 H, m), 9.17 (1 H, d, *J* 10 Hz), 10.93 (1 H, br), and 13.59 (1 H, br).

1-*Benzoylamino-4-(n-octylamino)anthraquinone* (2d), m.p. 159—159.5 °C (Found: C, 76.5; H, 6.5; N, 6.0. $C_{29}H_{30}N_2O_3$ requires C, 76.63; H, 6.65; N, 6.16%); $\lambda_{max.}$(benzene) 571 (ε 10 500) and 608 nm (9 200); δ_H (CDCl$_3$) 0.91 (3 H, t), 1.1—2.0 (12 H, m), 3.29 (2 H, q), 7.10 (1 H, d, *J* 10 Hz), 7.4—8.4 (9 H, m), 9.11 (1 H, d, *J* 10 Hz), 10.26 (1 H, br), and 13.47 (1 H, br).

1-*Benzoylamino-4-benzylaminoanthraquinone* (2e), m.p. 253.5—254.5 °C (Found: C, 77.8; H, 4.5; N, 6.1. $C_{28}H_{20}N_2O_3$ requires C, 77.76; H, 4.66; N, 6.48%); $\lambda_{max.}$(benzene) 563 (ε 11 300) and 596 nm (9 600); δ_H (CDCl$_3$) 4.64 (2 H, d), 7.21 (1 H, d, *J* 10 Hz), 7.36 (5 H, s), 7.4—8.5 (9 H, m), 9.16 (1 H, d, *J* 10 Hz), 10.75 (1 H, br), and 13.53 (1 H, br).

1-*Benzoylamino-4-cyclohexylaminoanthraquinone* (2f), m.p. 204—205 °C (Found: C, 76.2; H, 5.8; N, 6.3. $C_{27}H_{24}N_2O_3$ requires C, 76.40; H, 5.70; N, 6.60%); $\lambda_{max.}$(benzene) 573 (ε 11 200) and 612 nm (10 000); δ_H (CDCl$_3$) 1.0—2.3 (10 H, m), 3.6 (1 H, m), 7.21 (1 H, d, *J* 10 Hz), 7.4—8.5 (9 H, m), 9.14 (1 H, d, *J* 10 Hz), 10.56 (1 H, br), and 13.50 (1 H, br).

1-(p-*Nitrobenzoylamino*)-4-(n-butylamino)anthraquinone (2g), m.p. 234—234.5 °C (Found: C, 67.7; H, 4.9; N, 9.1. $C_{25}H_{21}N_3O_5$ requires C, 67.71; H, 4.77; N, 9.48%); $\lambda_{max.}$(benzene) 572 (ε 11 000) and 608 nm (9 500); δ_H (CDCl$_3$) 1.02 (3 H, t), 1.2—2.0 (4 H, m), 3.42 (2 H, q), 7.27 (1 H, d, *J* 10 Hz), 7.6—8.7 (8 H, m), 9.17 (1 H, d, *J* 10 Hz), 10.40 (1 H, br), and 13.76 (1 H, br).

1-*Acetylamino-4-(n-butylamino)anthraquinone* (2h), m.p. 134—134.5 °C (Found: C, 71.6; H, 5.9; N, 8.1. $C_{20}H_{20}N_2O_3$ requires C, 71.41; H, 5.99; N, 8.33%); $\lambda_{max.}$(benzene) 566 (ε 11 400) and 604 nm (9 700); δ_H (CDCl$_3$) 1.01 (3 H, t), 1.2—2.0 (4 H, m), 2.29 (3 H, s), 3.36 (2 H, q), 7.17 (1 H, d, *J* 10 Hz),

7.5—7.9 (2 H, m), 8.0—8.4 (2 H, m), 8.96 (1 H, d, J 10 Hz), 10.33 (1 H, br), and 12.53 (1 H, br).

1-*Propionylamino*-4-(*n-butylamino*)*anthraquinone* (2i), m.p. 153—154 °C (Found: C, 71.85; H, 6.5; N, 7.8. $C_{21}H_{22}N_2O_3$ requires C, 71.98; H, 6.33; N, 7.99%); $\lambda_{max.}$(benzene) 565 (ε 10 800) and 603 nm (9 500); δ_H (CDCl$_3$) 1.01 (3 H, t), 1.33 (3 H, t), 1.62 (4 H, m), 2.55 (2 H, q), 3.37 (2 H, q), 7.16 (1 H, d, J 10 Hz), 7.5—8.0 (2 H, m), 8.0—8.4 (2 H, m), 8.99 (1 H, d, J 10 Hz), 10.34 (1 H, br), and 12.55 (1 H, br).

1-*Butyrylamino*-4-(*n-butylamino*)*anthraquinone* (2j), m.p. 135—136.5 °C (Found: C, 72.7; H, 6.8; N, 7.6. $C_{22}H_{24}N_2O_3$ requires C, 72.51; H, 6.64; N, 7.69%); $\lambda_{max.}$(benzene) 565 (ε 10 700) and 603 nm (9 500); δ_H (CDCl$_3$) 1.00 (3 H, t), 1.05 (3 H, t), 1.2—2.2 (6 H, m), 2.51 (2 H, t), 3.38 (2 H, q), 7.17 (1 H, d, J 10 Hz), 7.5—8.0 (2 H, m), 8.0—8.5 (2 H, m), 9.01 (1 H, d, J 10 Hz), 10.36 (1 H, br), and 12.55 (1 H, br).

1-*Cinnamoylamino*-4-(*n-butylamino*)*anthraquinone* (2k), m.p. 231—232 °C (Found: C, 76.3; H, 5.6; N, 6.7. $C_{27}H_{24}N_2O_3$ requires C, 76.40; H, 5.70; N, 6.60%); $\lambda_{max.}$(benzene) 572 (ε 11 800) and 610 nm (10 300); δ_H (CDCl$_3$) 0.99 (3 H, t), 1.2—2.0 (4 H, m), 3.36 (2 H, q), 6.67 (1 H, d, J 16 Hz), 7.0—8.0 (9 H, m), 8.0—8.5 (2 H, m), 9.15 (1 H, d, J 10 Hz), 10.36 (1 H, br), and 12.89 (1 H, br).

4-(*n-Butylamino*)-1-*ethoxycarbonylaminoanthraquinone* (2l), m.p. 159—160 °C (Found: C, 69.0; H, 5.8; N, 7.4. $C_{21}H_{22}N_2O_4$ requires C, 68.84; H, 6.05; N, 7.64%); $\lambda_{max.}$(benzene) 563 (ε 11 100) and 600 nm (9 800); δ_H (CDCl$_3$) 1.00 (3 H, t), 1.36 (3 H, t), 1.2—2.0 (4 H, m), 3.38 (2 H, q), 4.25 (2 H, q), 7.18 (1 H, d, J 10 Hz), 7.5—7.9 (2 H, m), 8.0—8.4 (2 H, m), 8.76 (1 H, d, J 10 Hz), 10.26 (1 H, br), and 12.08 (1 H, br).

Quantum Yield Determinations.—The quantum yield of the photoamination of (1a) with butylamine was determined with monochromatic light (λ 435.8 nm) obtained through the following filter system: NaNO$_2$–H$_2$O and CuSO$_4$·5H$_2$O–aq. NH$_3$.[22] A potassium tris(oxalato)ferrate(III) solution was employed as the chemical actinometer.[23]

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