

## Photochemical Syntheses of Amino- and Hydroxy-1,4-naphthoquinones with High Selectivity

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A new route to amino- and hydroxy-naphthoquinones has been developed by the photochemical reaction of 5-aminonaphthoquinones with alkylamines. The regioselective syntheses of 8-alkylamino-5-aminonaphthoquinones were achieved under nitrogen in 90% yield. The selective and high yielding syntheses of 8-hydroxy-5-aminonaphthoquinones were achieved under aerated conditions using *t*-butylamine as a good oxygen carrier.

Although photochemically induced nucleophilic substitution reactions of quinone systems are well documented,<sup>1-4</sup> few for aminonaphthoquinones are known. Some photochemical reactions of methoxynaphthoquinones with amines to give the corresponding aminonaphthoquinones and methoxy(amino)-naphthoquinones are known,<sup>5-7</sup> but not those for aminonaphthoquinones with amines. Recently we reported that the photochemical reaction of 1-acylaminoanthraquinones with alkylamines gave selectively 4-alkylamino derivatives in good yields.<sup>8</sup>

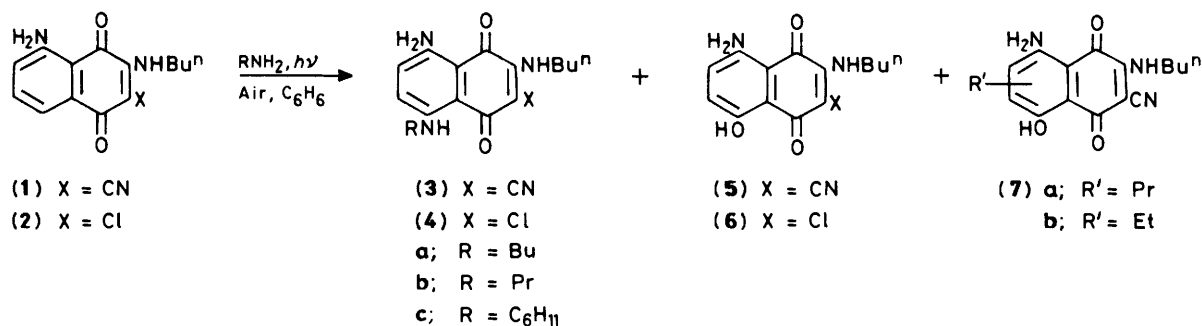
In our previous paper,<sup>9</sup> we reported the novel and regioselective photochemical syntheses of 8-alkylamino- and 8-hydroxy-5-amino-naphthoquinones by the reaction of 5-aminonaphthoquinones with alkylamines under nitrogen and aerated conditions, respectively. In this paper we report the details of the photochemical reactions between 5-aminonaphthoquinones and various amines to synthesize a variety of aminonaphthoquinone derivatives which are poorly synthesized by thermal reactions.

### Results and Discussion

**Photochemical Reaction of 5-Aminonaphthoquinones with *n*-Butylamine.**—The photochemical reaction of 5-amino-3-butylamino-2-cyano-1,4-naphthoquinone (1) with *n*-butylamine in aerated benzene gave a mixture of products, 8-butylamino-(3a), 8-hydroxy- (5), and 8-hydroxy-6(or 7)-propyl-5-amino-3-butylamino-2-cyano-1,4-naphthoquinone (7a), respectively (Scheme). None of these reactions proceeded under thermal

1, run 1). We propose that atmospheric oxygen co-operates with the amine in the direct hydroxylation of (1). Hydroxylation did not proceed in the absence of amine. The photochemical reaction of (5) with *n*-butylamine under aerated conditions gave compound (7a) in 26% yield, and the formation of (7a) is proposed to follow by further alkylation of (5). The first absorption bands of (5) were observed at 540 and 580 nm, and the formation of (7a) was completely suppressed using irradiation over the range 400–500 nm. Introduction of an amino or hydroxy group to the benzenoid ring of 1,4-naphthoquinones is a very important synthetic method for the preparation of some naphthoquinone derivatives which are only poorly synthesized by thermal reactions. Recently we prepared (3a) by the metal-promoted direct 8-alkylation of (1) in 22% yield.<sup>10</sup> The direct hydroxylation of the benzenoid ring of 1,4-naphthoquinones is not known but the reductive hydroxylation of 5-nitronaphthoquinones to give 5-amino-8-hydroxynaphthoquinones has been reported.<sup>11</sup> The photochemical alkylation of (5) by alkylamines to give (7) may be the first example in which the carbon-chain length of the alkyl group of an amine is reduced as shown in the Scheme. The details of this photochemical alkylation were not examined. Hereafter, selective syntheses of (3) and (5) are examined.

**Selective Syntheses of 8-Alkylaminonaphthoquinones.**—When a benzene solution of (1) and *n*-butylamine purged with nitrogen, was irradiated with Pyrex-filtered light from a high-pressure mercury lamp, the colour of the solution turned from initial orange to deep blue. The change in the visible spectrum of



Scheme.

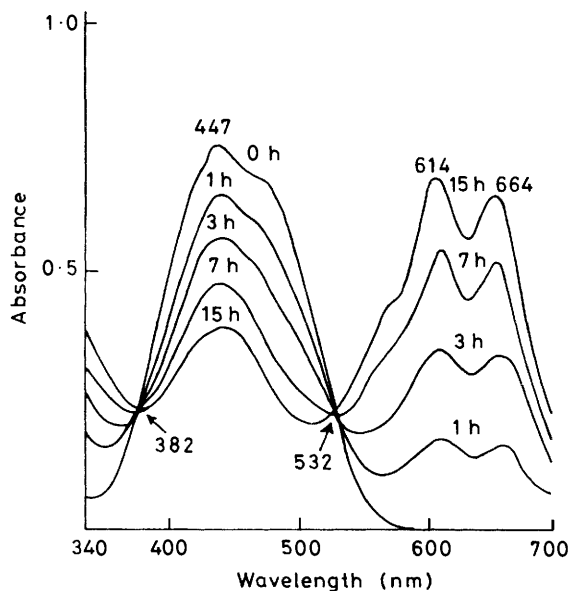
conditions. Regioselective 8-alkylation and 8-hydroxylation of (1) are competing reactions under aerated conditions. The reaction was found to occur by the absorption of the light corresponding to the first absorption band of compound (1) ( $\lambda_{\text{max}}$ , 447 nm). Compounds (5) and (7a) were not formed under a nitrogen atmosphere, and (3a) was obtained selectively (Table

the benzene solution of (1) with *n*-butylamine is shown in Figure 1. The absorbance at 447 nm, characteristic of (1), decreased with increasing irradiation time and new double-headed peaks, characteristic of (3a), appeared at 614 nm and 664 nm, and isosbestic points were observed at 382 nm and 532 nm. After the reaction (3a) was selectively obtained in 62% yield

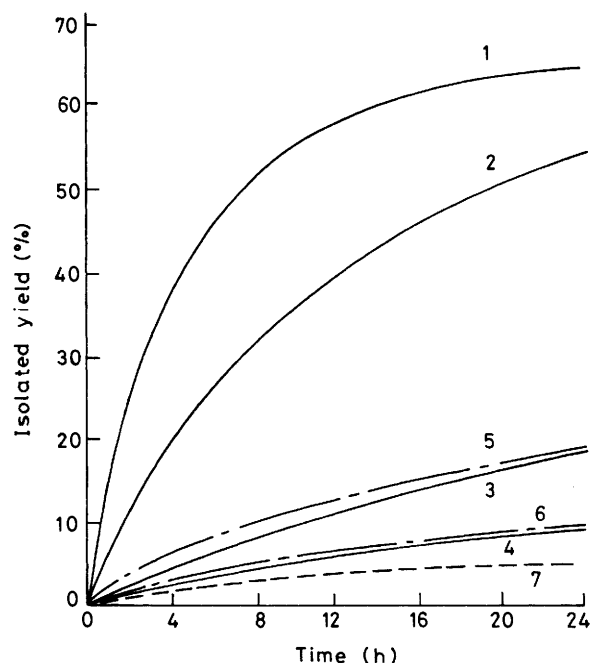
**Table 1.** Photochemical reaction of 5-aminonaphthoquinones with amines under nitrogen<sup>a</sup>

Run	Substrate	Amine	Time (h)	Substrate recovery (%)	Products (Yield/%) <sup>b</sup>
1	(1)	Bu <sup>n</sup> NH <sub>2</sub>	12	32	(3a) 62 (91) <sup>c</sup>
2	(1)	Bu <sup>n</sup> NH <sub>2</sub>	48	13	(3a) 71 (82) <sup>c</sup>
3	(1)	Pr <sup>n</sup> NH <sub>2</sub>	12	56	(3b) 43 (98) <sup>c</sup>
4	(1)	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	24	33	(3c) 24 (36) <sup>c</sup>
5	(1)	Bu <sup>t</sup> NH <sub>2</sub>	12	77	0
6	(1)	Et <sub>2</sub> NH	8	0	0
7	(1)	PhNH <sub>2</sub>	5	62	0
8	(2)	Bu <sup>n</sup> NH <sub>2</sub>	24	27	(4a) 19 (26) <sup>c</sup>

<sup>a</sup> Substrate = 0.3 mmol, amine = 30 mmol, benzene = 300 ml. Irradiation with 100 W high-pressure mercury lamp at 30 °C. Irradiation wavelength  $\geq$  300 nm. <sup>b</sup> Isolated yield after chromatography. <sup>c</sup> Yield based on amount of substrate consumed.

**Figure 1.** Visible spectral changes of the photoamination of (1) with n-butylamine in benzene under nitrogen at 30 °C. [(1)] = 1 mM, [n-butylamine] = 0.1 M.

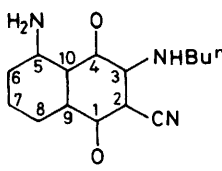
together with 32% recovery of (1) (Table 1, run 1). T.l.c. analysis (silica gel; benzene) showed that (5) and (7) were not produced under the reaction conditions. The quantum yield of the photochemical reaction of (1) with n-butylamine under nitrogen was *ca.*  $1.3 \times 10^{-4}$  {[n-butylamine]/[(1)] = 500}. A longer reaction time increased the isolated yield of (3a) but decreased the yield based on the amount of (1) consumed, owing to the further photochemical decomposition of (3a) (run 2). Similar reaction of (1) with n-propylamine gave (3b) in 98% yield (from substrate consumed) (run 3), but with cyclohexylamine the yield of (3c) was depressed to 36% (from substrate consumed) (run 4). The reaction of (1) with t-butylamine did not give the aminated product (run 5). Diethylamine and triethylamine did not give the aminated product but accelerated the photodecomposition of (1) (run 6). Aniline did not react with (1) (run 7). The reaction of 5-amino-3-butylamino-2-chloro-1,4-naphthoquinone (2) with n-butylamine gave the corresponding 8-butylamino derivative (4a) in 26% yield (from substrate consumed) (run 8). The reactivity of (2) was less than that of (1), and (2) gradually decomposed

**Figure 2.** Solvent effect on the yield of (3a) in the reaction of (1) with n-butylamine under nitrogen at 30 °C. [(1)] = 1 mM, [n-butylamine] = 0.1 M. Solvent: B = benzene, A = acetonitrile, P = propan-2-ol, E = ethanol. Solvent systems (volume percent in benzene): 1, B; 2, A-B (10%); 3, A-B (50%); 4, A; 5, P-B (25%); 6, P-B (50%); 7, E-B (50%).

under the reaction conditions. The effect of solvents on the formation of (3a) is shown in Figure 2. In benzene-acetonitrile systems, the addition of acetonitrile greatly decreased the isolated yield of (3a) but the yield based on the amount of (1) consumed did not vary so much after the prolonged reaction time, and consequently the addition of acetonitrile retarded the rate of amination. Similar results were also obtained when ethanol or propan-2-ol were added to the reaction mixture. The reaction of (1) with n-butylamine in ethanol did not proceed and (3a) was not obtained even after 24 h. It was found that polar solvents greatly retarded the direct photoamination of (1).

The regioselective 8-alkylation of (1) can be explained by the frontier orbital method by which we rationalized the regioselective 4-alkylation of 1-acylaminoanthraquinones.<sup>8</sup> The  $\pi$ -electron densities for the HOMO and the LUMO of (1) were calculated by means of the Pariser-Parr-Pople (PPP) method<sup>12</sup> with variable  $\beta, \gamma$  approximations<sup>13</sup> and the results are shown in Table 2. The results suggest that the photoamination is expected to occur at the 8-position which has the highest electron density in the HOMO (HOMO-controlled). Details of the reaction mechanism were not studied.

**Selective Syntheses of 8-Hydroxynaphthoquinones.**—The regioselective 8-hydroxylation of the benzenoid ring of 5-aminonaphthoquinones was achieved by the photochemical reaction of (1) with amines under aerated conditions (Table 3, run 1). It was necessary to depress the formation of (3) for the selective synthesis of (5). The addition of a polar solvent such as acetonitrile greatly retarded the formation of (3) (Figure 2). The formation of (3a) was completely suppressed by addition of acetonitrile to a benzene solution (in 33 vol. %), but the yield of (5) was poor (run 4). The possible formation of (7) could be excluded using the irradiation range up to 500 nm, and later experiments (Table 3, runs 6–12) were conducted in the

**Table 2.** Calculated  $\pi$ -electron densities for the HOMO and LUMO of (1)


	HOMO	LUMO
C(1)	0.004	0.121
C(2)	0.035	0.092
C(3)	0.001	0.241
C(4)	0.056	0.355
C(5)	0.055	0.059
C(6)	0.254	0.100
C(7)	0.003	0.108
C(8)	0.340 <sup>a</sup>	0.063
C(9)	0.066	0.123
C(10)	0.324	0.007

<sup>a</sup> Observed reaction site.

irradiation range 400–500 nm using the solution filter system.<sup>14</sup>

The selective synthesis of compounds (5) could be achieved using secondary or tertiary alkylamines but the yields of (5) were poor (Table 3, runs 7–9). The selective and high yielding synthesis of (5) was achieved using *t*-butylamine under aerated conditions (run 10). The quantum yield of the photohydroxylation by the reaction of (1) with *t*-butylamine was *ca.*  $1.2 \times 10^{-3}$   $\{[t\text{-butylamine}]/[(1)] = 500\}$ . Similar reaction of (2) with *n*-butylamine only gave (6) in 32% yield, but with *t*-butylamine (6) was obtained in 82% isolated yield (run 12). Butylamine did not react with (1) or (2) and is a good oxygen carrier for the preparation of (5) or (6).

## Experimental

M.p.s are uncorrected. U.v.–visible and mass spectra were obtained with a Hitachi EPS-3T spectrophotometer and a Hitachi RMU-6E mass spectrometer, respectively. <sup>1</sup>H N.m.r. spectra were obtained with a Hitachi Perkin-Elmer R-20 spectrometer using SiMe<sub>4</sub> as internal standard. Elemental analyses were recorded on a Yanaco CHN recorder MT-2.

Starting materials (1) and (2) were prepared using the same method described in the literature<sup>15</sup> 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 usual methods.

5-Amino-3-butylamino-2-cyano-1,4-naphthoquinone (1): m.p. 153–156 °C (from benzene) (Found: C, 67.1; H, 5.75; N, 16.0. Calc. for C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>: C, 66.90; H, 5.61; N, 15.60%);  $\lambda_{\text{max}}$  (benzene) 418sh ( $\epsilon$  5 900), 447 (7 100), and 484sh nm (6 200);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 0.96 (3 H, t), 1.20–1.78 (4 H, m), 3.81 (2 H, q), 6.77 (5-NH<sub>2</sub>, br), 6.80 (1 H, dd, *J* 8, *J'* 2 Hz), 7.14 (3-NH, br), and 7.25–7.55 (2 H, m); *m/z* 269 (*M*<sup>+</sup>, 80%), 240 (27), and 226 (100).

5-Amino-3-butylamino-2-chloro-1,4-naphthoquinone (2): m.p. 127–129 °C (from benzene) (Found: C, 60.9; H, 5.5; N, 10.75. Calc. for C<sub>14</sub>H<sub>15</sub>ClN<sub>2</sub>O<sub>2</sub>: C, 60.33; H, 5.42; N, 10.05%);  $\lambda_{\text{max}}$  (benzene) 458nm ( $\epsilon$  8 000);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 0.98 (3 H, t), 1.28–1.73 (4 H, m), 3.82 (2 H, q), 6.42 (3-NH, br), 6.78 (5-NH<sub>2</sub>, br), 6.90 (1 H, d d, *J* 8, *J'* 2 Hz), 7.38 (1 H, d, *J* 8 Hz), and 7.63 (1 H, dd, *J* 8, *J'* 2 Hz); *m/z* (rel. intensity) 280 [*M*<sup>+</sup> (<sup>37</sup>Cl), 21%], 278 [*M*<sup>+</sup> (<sup>35</sup>Cl), 53], 237 (36), and 235 (100).

**Table 3.** Photochemical reaction of 5-aminonaphthoquinones with amines under aerated conditions<sup>a</sup>

Run	Substrate	Solvent <sup>b</sup>	Amine	Products (yield/%) <sup>c</sup>
1 <sup>d</sup>	(1)	B	Bu <sup>n</sup> NH <sub>2</sub>	(3a) 7, (5) 28, (7a) 11
2 <sup>d</sup>	(1)	A/B (10) <sup>e</sup>	Bu <sup>n</sup> NH <sub>2</sub>	(3a) 9, (5) 36, (7a) 11
3 <sup>d</sup>	(1)	A/B (20) <sup>e</sup>	Bu <sup>n</sup> NH <sub>2</sub>	(3a) 1, (5) 34, (7a) 13
4 <sup>d</sup>	(1)	A/B (33) <sup>e</sup>	Bu <sup>n</sup> NH <sub>2</sub>	(3a) 0, (5) 32, (7a) 19
5 <sup>d</sup>	(1)	B	Pr <sup>n</sup> NH <sub>2</sub>	(3b) 1, (5) 32, (7b) 9
6 <sup>f</sup>	(1)	B	C <sub>6</sub> H <sub>11</sub> NH <sub>2</sub>	(5) 50
7 <sup>f</sup>	(1)	B	Et <sub>2</sub> NH	(5) 26
8 <sup>f</sup>	(1)	B	C <sub>5</sub> H <sub>10</sub> NH	(5) 30
9 <sup>f</sup>	(1)	B	Et <sub>3</sub> N	(5) 7
10 <sup>f</sup>	(1)	B	Bu <sup>n</sup> NH <sub>2</sub>	(5) 81 (87) <sup>g</sup>
11 <sup>f</sup>	(2)	A/B (33) <sup>e</sup>	Bu <sup>n</sup> NH <sub>2</sub>	(6) 32 (48) <sup>g</sup>
12 <sup>f</sup>	(2)	B	Bu <sup>n</sup> NH <sub>2</sub>	(6) 82 (99) <sup>g</sup>

<sup>a</sup> Substrate = 0.3 mmol, amine = 30 mmol, solvent = 300 ml. Irradiation with 100 W high-pressure mercury lamp at 30 °C for 12 h.

<sup>b</sup> A = acetonitrile, B = benzene. <sup>c</sup> Isolated yield after chromatography.

<sup>d</sup> Irradiation wavelength  $\geq$  300 nm. <sup>e</sup> Acetonitrile volume percent in benzene. <sup>f</sup> Irradiation wavelength +400–500 nm. <sup>g</sup> Yield determined by spectrophotometry.

**Photochemical Reaction of (1) with Amines. General Procedure.**—A solution of substrate (0.3 mmol) and amine (30 mmol) in a solvent (300 ml) was irradiated under nitrogen or aerated conditions at 30 °C using a 100 W high-pressure mercury lamp equipped with a Pyrex cooling jacket. The irradiation range from 400 to 500 nm was obtained through the filter system.<sup>14</sup> All the photoreactions were monitored by visible spectroscopy and t.l.c. After the reaction, the solvent was removed under reduced pressure. Aqueous hydrochloric acid (pH 1; 100 ml) was added to the residue and the resulting precipitate was filtered off, dried, and separated by column chromatography [silica gel (Wakogel C-300); benzene]. The products were purified by recrystallization. The structures were confirmed from the data shown below.

5-Amino-3,8-bis(*butylamino*)-2-cyano-1,4-naphthoquinone (3a): m.p. 186–187 °C (from benzene) (Found: C, 66.55; H, 7.15; N, 16.05. C<sub>19</sub>H<sub>24</sub>N<sub>4</sub>O<sub>2</sub> requires C, 67.04; H, 7.11; N, 16.46%);  $\lambda_{\text{max}}$  (benzene) 565sh ( $\epsilon$  6 000), 612 (11 000), and 660 nm (10 300);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 0.94 (3 H, t), 0.98 (3 H, t), 1.24–1.76 (8 H, m), 3.26 (2 H, q), 3.79 (2 H, q), 6.73 (3-NH, br), 6.78 (5-NH<sub>2</sub>, br), 7.06 (1 H, d, *J* 8 Hz), 7.14 (1 H, d, *J* 8 Hz), and 10.26 (8-NH, br); *m/z* 340 (*M*<sup>+</sup>, 49%) and 297 (100).

5-Amino-3-butylamino-2-cyano-8-propylamino-1,4-naphthoquinone (3b): m.p. 188–189 °C (from benzene) (Found: C, 66.2; H, 6.9; N, 16.95. C<sub>18</sub>H<sub>22</sub>N<sub>4</sub>O<sub>2</sub> requires C, 66.24; H, 6.79; N, 17.17%);  $\lambda_{\text{max}}$  (benzene) 440 ( $\epsilon$  3 300), 612 (11 100), and 662 nm (10 300);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 0.90–1.14 (6 H, m), 1.17–1.90 (6 H, m), 3.30 (2 H, q), 3.90 (2 H, q), 7.01 (1 H, d, *J* 8 Hz), 7.09 (3-NH, br), 7.47 (1 H, d, *J* 8 Hz), 7.50 (5-NH<sub>2</sub>, br), and 10.63 (8-NH, br); *m/z* 326 (*M*<sup>+</sup>, 31%), 298 (22), and 297 (100).

5-Amino-3-butylamino-2-cyano-8-cyclohexylamino-1,4-naphthoquinone (3c): m.p. 212–215 °C (from benzene) (Found: C, 68.5; H, 7.1; N, 15.95. C<sub>21</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub> requires C, 68.85; H, 6.83; N, 15.30%);  $\lambda_{\text{max}}$  (benzene) 441 ( $\epsilon$  2 700), 569 (4 700), 613 (8 600), and 663 nm (8 600);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 0.95 (3 H, t), 1.25–2.15 (15 H, m), 3.85 (2 H, q), 6.84 (1 H, d, *J* 8 Hz), 6.90 (3-NH, br), 7.30 (1 H, d, *J* 8 Hz), 7.49 (5-NH<sub>2</sub>, br), and 10.55 (8-NH, br); *m/z* 366 (*M*<sup>+</sup>, 100%), 349 (13), 324 (41), and 323 (78).

5-Amino-3,8-bis(*butylamino*)-2-chloro-1,4-naphthoquinone (4a): m.p. 149–150 °C (from benzene) (Found: C, 61.4; H, 7.05; N, 11.85. C<sub>18</sub>H<sub>24</sub>ClN<sub>3</sub>O<sub>2</sub> requires C, 61.80; H, 6.91; N, 12.01%);  $\lambda_{\text{max}}$  (benzene) 550sh ( $\epsilon$  6 000), 595 (12 000), and 642 nm (13 000);  $\delta_{\text{H}}$ (CDCl<sub>3</sub>) 0.98 (6 H, t), 1.25–1.75 (8 H, m), 3.35 (2 H, q), 3.86 (2 H, q), 6.19 (5-NH<sub>2</sub>, br), 6.90 (1 H, d, *J* 8 Hz), 7.20 (3-

NH, br), 7.88 (1 H, d,  $J$  8 Hz), and 10.60 (8-NH, br);  $m/z$  351 [ $M^+$  ( $^{37}\text{Cl}$ )], 33%, 349 [ $M^+$  ( $^{35}\text{Cl}$ )], 100], 308 (17), and 306 (100).

**5-Amino-3-butylamino-2-cyano-8-hydroxy-1,4-naphthoquinone (5):** m.p. 217–217.5 °C (from benzene) (Found: C, 62.95; H, 5.2; N, 14.45.  $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}_3$  requires C, 63.16; H, 5.26; N, 14.74%);  $\lambda_{\text{max}}$  (benzene) 510 ( $\epsilon$  6 200), 540 (8 300), and 580 nm (6 000);  $\delta_{\text{H}}[(\text{CD}_3)_2\text{SO}]$  0.91 (3 H, t), 1.18–1.78 (4 H, m), 3.66 (2 H, q), 7.05 (2 H, s), 8.31 (5-NH<sub>2</sub>, br), 8.76 (3-NH, br), and 13.31 (8-OH, br);  $m/z$  285 ( $M^+$ , 100%), 256 (31), and 242 (86).

**5-Amino-3-butylamino-2-chloro-8-hydroxy-1,4-naphthoquinone (6):** m.p. 146–147 °C (from benzene) (Found: C, 56.75; H, 5.25; N, 9.4.  $\text{C}_{14}\text{H}_{15}\text{ClN}_2\text{O}_3$  requires C, 57.05; H, 5.13; N, 9.50%);  $\lambda_{\text{max}}$  (benzene) 497 ( $\epsilon$  6 900), 525 (7 000), and 558 nm (5 000);  $\delta_{\text{H}}(\text{CDCl}_3)$  0.95 (3 H, t), 1.31–1.81 (4 H, m), 3.82 (2 H, q), 6.41 (3-NH, br), 6.65 (1 H, d,  $J$  8 Hz), 6.74 (5-NH<sub>2</sub>, br), 6.99 (1 H, d,  $J$  8 Hz), and 13.57 (8-OH, s);  $m/z$  296 [ $M^+$  ( $^{37}\text{Cl}$ )], 18%, 294 [ $M^+$  ( $^{35}\text{Cl}$ )], 51], 253 (41), and 251 (100).

**5-Amino-3-butylamino-2-cyano-8-hydroxy-6(or 7)-propyl-1,4-naphthoquinone (7a):** m.p. 195–197 °C (from hexane) (Found: C, 65.9; H, 6.15; N, 13.5.  $\text{C}_{18}\text{H}_{21}\text{N}_3\text{O}_3$  requires C, 66.03; H, 6.48; N, 12.84%);  $\lambda_{\text{max}}$  (benzene) 510sh, 540, and 580 nm;  $\delta_{\text{H}}(\text{CDCl}_3)$  0.90–1.08 (6 H, m), 1.17–1.90 (6 H, m), 3.24–3.44 (4 H, m), 7.33–7.84 (4 H, m), and 14.67 (8-OH, br);  $m/z$  327 ( $M^+$ , 56%), 298 (24), 285 (35), and 284 (100).

**5-Amino-3-butylamino-2-cyano-6(or 7)-ethyl-8-hydroxy-1,4-naphthoquinone (7b):**  $\lambda_{\text{max}}$  (benzene) 510sh, 540, and 578 nm;  $m/z$  313 ( $M^+$ , 100%), 284 (44), and 270 (88).

**Quantum Yield Determination.**—The quantum yields of the photoreactions were determined using the irradiation wavelength ( $\lambda_{\text{max}}$ , 435.8 nm) of a high-pressure mercury lamp obtained *via* the following filter system:  $\text{NaNO}_2\text{-H}_2\text{O}$  and  $\text{CuSO}_4\cdot 5\text{H}_2\text{O-NH}_4\text{OH}$ .<sup>14</sup> A potassium tris(oxalato)ferrate(III) solution was employed as the chemical actinometer.<sup>16</sup>

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