Photoamination of 1-hydroxyanthraquinones

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Abstract

Photoamination of 1-hydroxyanthraquinone with *n*-butylamine gave not only 1-hydroxy-4-(butylamino)anthraquinone (**5**) but also 1-hydroxy-2-(butylamino)anthraquinone (**6**) in contrast with the amination of 1-aminoanthraquinones where only 4-amination occurs. The production ratio of **6** to **5** was 0.2 in the reaction under air using acetonitrile and mixtures of acetonitrile and water as solvents. On the other hand, in the reaction under nitrogen the ratio increased from 0.2 to 3.2 as the water content of the solvent increased from 0 to 50 vol.%. The reaction of 1-hydroxy-2-bromoanthraquinone and 1-hydroxy-2,4-bromoanthraquinone gave 1-hydroxy-2-bromo-4-(butylamino)anthraquinone only. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Photoamination; 1-Hydroxyanthraquinone; Product distribution

1. Introduction

The photochemical behavior of anthraquinone derivatives has been studied for a long time with respect to the photofading of vat dyes and photosensitized oxidation [1–5]. Since the object of those studies, however, was restricted to hydrogen abstraction by an excited carbonyl group and since intense interest has been generated concerning photoreduction via the lowest triplet nπ* state, anthraquinone and its derivatives having electron-withdrawing substituents have been accepted as reactive. On the other hand, the photoreactivity of derivatives having electron-donating substituents has been considered very low because their lowest excited states are intramolecular CT states inactive for hydrogen abstraction [1–5].

In the area of photosubstitution, few examples has been reported for the derivatives having electron-withdrawing substituents [6–17] and several reports have been presented for the derivatives having electron-donating substituents [20–27] including our report on the photoamination of sodium 1-amino-4-bromoanthraquinone-2-sulfonate [18,19]. The functional group is substituted by hydroxide ion [20] and an amine [21–23], and a hydrogen of the anthraquinone skeleton is also substituted by an amine [21,22] in methoxyanthraquinones. The radical arising from hydroxide ion is considered to be responsible for the hydroxylation [20] and the amination is regarded as nucleophilic substitu-

tion [21,22]. Sulfonation occurs at the 2-position of 1-aminoanthraquinone and at the 2- and 4-position of 1-hydroxyanthraquinone [24–26]. Sulfite radical anion arising from sulfite ion is considered to attack the ground state of the quinones. Furthermore, 1- and 2-hydroxyanthraquinone are also substituted by an amine [27]. The hydrogen at the peri-position is reactive as amination occurs at the 4-position in 1-hydroxyanthraquinone and at the 1-position in 2-hydroxyanthraquinone.

We have already clarified the mechanism of the photoamination of haloaminoanthraquinones including sodium 1-amino-4-bromoanthraquinone-2-sulfonate [28–31]. In this paper, we report on the photoamination of 1-hydroxyanthraquinone and 1-hydroxyhaloanthraquinones, where different behavior from that of the haloaminoanthraquinones has been observed. Amination at the 2-position has been newly discovered.

2. Experimental

2.1. Materials

1-Acetylaminoanthraquinone (**1a**) and 1-acetylamino-4-bromoanthraquinone (**1b**) were prepared by the acetylation of 1-aminoanthraquinone (**2a**) and 1-amino-4-bromoanthraquinone (**2b**), respectively (Scheme 1). The acetylation products **1a** and **1b** were purified by recrystallization from toluene and from a mixture of toluene and ethanol (1:1), respectively [30]. 1-Amino-4-bromoanthraquinone

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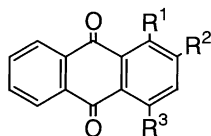
1 **a**: R^1 = NHCOCH$_3$, R^2 = R^3 = H
  b: R^1 = NHCOCH$_3$, R^2 = H, R^3 = Br
2 **a**: R^1 = NH$_2$,   R^2 = R^3 = H
  b: R^1 = NH$_2$,   R^2 = H, R^3 = Br
3 **a**: R^1 = OH,   R^2 = R^3 = H
  b: R^1 = OH,   R^2 = Br, R^3 = H
  c: R^1 = OH,   R^2 = R^3 = Br
4   R^1 = OH,   R^2 = Br, R^3 = NHC$_4$H$_9$
5   R^1 = OH,   R^2 = H, R^3 = NHC$_4$H$_9$
6   R^1 = OH,   R^2 = NHC$_4$H$_9$, R^3 = H

Scheme 1.

(**2b**) was synthesized by the desulfonation of sodium 1-amino-4-bromoanthraquinone-2-sulfonate in aqueous sulfuric acid and purified by silica gel column chromatography using benzene as an eluent and recrystallization from acetic acid; m.p. 175.7–176.6°C. Found: C, 55.78; H, 2.50; N, 4.64%. Calcd for $C_{14}H_8NO_2Br$: C, 55.65; H, 2.67; N, 4.64%. 1-Hydroxyanthraquinone (**3a**) was obtained by the diazotization of **2a** followed by decomposition in aqueous sulfuric acid solution and purified by silica gel column chromatography using benzene as an eluent and recrystallization from benzene; m.p. 194.0–195.6°C. Found: C, 74.82; H, 3.68%. Calcd for $C_{14}H_8O_3$: C, 75.39; H, 3.60%. 1-Hydroxy-2-bromoanthraquinone (**3b**) and 1-hydroxy-2,4-dibromoanthraquinone (**3c**) were prepared by the bromination of **3a**. Compound **3b** was recrystallized from a 1:1 benzene–ethanol mixture; m.p. 201.7–202.3°C. Found: C, 55.48; H, 2.29%. Calcd for $C_{14}H_7O_3Br$: C, 55.48; H, 2.33%. Compound **5c** was recrystallized from acetic acid; m.p. 242.6–243.7°C. Found: C, 44.26; H, 1.48%. Calcd for $C_{14}H_6O_3Br_2$: C, 44.02; H, 1.58%. Guaranteed reagent grade *n*-butylamine (Tokyo Kasei) was used without further purification. Ethanol was dried and fractionally distilled. Isobutyronitrile of 99% purity was purchased from Aldrich Chemical and used without further purification. Other solvents used were of Kanto Kagaku's UGR grade.

2.2. Procedures

Light irradiation was carried out with a 500 W high-pressure mercury lamp through appropriate glass or interference filters. Amination products of **3a** were determined using a Shimadzu HPLC system. The amount of amination product from **3b** and **3c** was determined from the visible absorption spectra of the irradiated solution. The quantum yield of the reaction was determined in comparison with the photoamination of 1-amino-2,4-dibromoanthraquinone [31] in aerated ethanol ($\Phi = 1.7 \times 10^{-3}$, [butylamine] = 5.0×10^{-2} mol dm^{-3}). Visible absorption spectra were recorded using a Shimadzu UV-200 spectrophotometer. Measurement of NMR spectra was made with a Hitachi

R-24 (60 MHz) spectrometer. The mass spectra were measured using a JEOL DX-300 mass spectrometer.

2.3. Amination products

After evaporating the solvent from the irradiated acetonitrile solutions of **3**, the amination products were separated using a silica gel column with benzene as the eluent, and then recrystallized from acetonitrile.

1. 1-Hydroxy-2-bromo-4-(butylamino)anthraquinone (**4**): m.p. 132.0–132.4°C. Found: C, 57.77; H, 4.24; N, 3.75%; M$^+$, 373, 375. Calcd for $C_{18}H_{16}NO_3Br_2$: C, 57.77; H, 4.31; N, 3.74%; M$^+$, 373, 375. 1H NMR (CDCl$_3$) $\delta = 0.99$ (3H, t, $J = 6$ Hz, CH$_3$), 1.65 (4H, m, (CH$_2$)$_2$), 3.23 (2H, dt, $J = 6$ and 6 Hz, NCH$_2$), 7.41 (1H, s), 7.71 (2H, m), 8.27 (2H, m), 9.9–10.3 (1H, NH), 14.27 (1H, s, OH).
2. 1-Hydroxy-4-(butylamino)anthraquinone (**5**): m.p. 127.3–128.0°C. Found: C, 73.14; H, 5.70; N, 4.52%; M$^+$, 295. Calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74%; M$^+$, 295. 1H NMR (CDCl$_3$) $\delta = 0.99$ (3H, t, $J = 6$ Hz, CH$_3$), 1.65 (4H, m, (CH$_2$)$_2$), 3.23 (2H, dt, $J = 6$ and 6 Hz, NCH$_2$), 7.12 (2H, s), 7.71 (2H, m), 8.27 (2H, m), 10.2–10.7 (1H, NH), 13.70 (1H, s, OH).
3. 1-Hydroxy-2-(butylamino)anthraquinone (**6**): m.p. 160.0–160.8°C. Found: C, 73.30; H, 5.67; N, 4.47%; M$^+$, 295. Calculated values are the same as those for **5**. 1H NMR (CDCl$_3$) $\delta = 0.99$ (3H, t, $J = 6$ Hz, CH$_3$), 1.65 (4H, m, (CH$_2$)$_2$), 3.23 (2H, dt, $J = 6$ and 6 Hz, NCH$_2$), 5.10 (1H, t, $J = 6$ Hz, NH), 6.65 (1H, d, $J = 9$ Hz), 7.71 (3H, m), 8.22 (2H, m), 13.31 (1H, s, OH).

3. Results and discussion

3.1. Acid–base equilibrium in the ground state

In the presence of an amine, 1-hydroxyanthraquinones (**3a–c**) are in equilibrium with the phenoxide form (base form). The values of relative measure for acidity of the 1-hydroxyanthraquinones (**3a–c**) showed that **3b** and **3c** are stronger acids than **3a** because of the electron-withdrawing effect of the bromine atom (Table 1). The absorption spectra of **3b** in ethanol are shown in Fig. 1. A very small amount of concentrated hydrochloric acid was added to the solution of 1-hydroxyanthraquinones (**3a–c**) to obtain visible absorption spectra of their acid forms. The 1-hydroxyanthraquinones (**3a–c**) were dissociated completely by adding sodium hydroxide on measuring visible absorption spectra of their base forms.

3.2. Anomalous behavior of the photoamination of 1-hydroxyanthraquinones

When **3a** (1.00×10^{-4} mol dm^{-3}) and *n*-butylamine (5.00×10^{-2} mol dm^{-3}) in aerated acetonitrile, where the

Table 1
Acid–base equilibrium of 1-hydroxyanthraquinones in the presence of *n*-butylamine at 25°C[a]

Solvent	K (dm^3 mol^{-1})	Ethanol		K (dm^3 mol^{-1})	Acetonitrile	
		λ_{max} of AQOH (nm)	λ_{max} of AQO$^-$ (nm)		λ_{max} of AQOH (nm)	λ_{max} of AQO$^-$ (nm)
3a	0.676±0.056	403	496	(4.43±0.17)×10^{-2}	401	524
3b	56.8±4.6	408	503	3.55±0.05	405	527
3c	216±20	415	504	13.6±0.3	413	528

[a] $K = $ [AQO$^-$]/[AQOH][*n*-butylamine]; AQOH: acid form; AQO$^-$: base form.

hydroxyl group of **3a** was little dissociated, were irradiated by light of $\lambda > 400$ nm, both 1-hydroxy-4-(butylamino)-anthraquinone (**5**) and 1-hydroxy-2-(butylamino)anthraqui-none (**6**) were obtained in the ratio of 5:1. While Studinskii et al. [27] have reported that only the 4-position of 1-hydroxyanthraquinone was aminated, we have newly discovered 2-amination in addition to 4-amination. They used a DMF–water mixture as a solvent and we used aceto-nitrile. The difference in solvent may result in a different product distribution.

In the case of **3b** and **3c**, where the hydroxyl groups of these compounds were dissociated to some extent and the oxyanions of **3b** and **3c** were also excited in contrast to the case of **3a**, photoamination afforded the same prod-uct, 1-hydroxy-2-bromo-4-(butylamino)anthraquinone (**4**) alone. The product obtained from **3c** was identified by comparison of its electronic spectrum and R_f-value (TLC) with those of **4** obtained from **3b**. The reactions of both **3b** and **3c** saturated faster than the reaction of **3a** (Fig. 2). The values of yield/conversion in the cases of **3a**, **3b** and **3c** were independent of irradiation time and were 0.56, 0.73 and 0.37, respectively. The reaction of **3b** is most efficient from a synthetic point of view.

While the hydroxyl group of **3a** was little dissociated in acetonitrile under the amine concentration of 5.00×10^{-2} mol dm^{-3}, the degree of dissociation of the hydroxyl group becomes about 0.4 in acetonitrile containing 30 vol.%

Fig. 2. Yield of **5** + **6** (for **3a**) and **4** (for **3b** and **3c**) in the photoamination of 1-hydroxyanthraquinones in acetonitrile under air. Excitation wavelength: $\lambda > 400$ nm; [**3**] = 1.0×10^{-4} mol dm^{-3}; [*n*-butylamine] = 5.0×10^{-2} mol dm^{-3}; (●) **5** + **6** for **3a**; (■) **4** for **3b**; (▲) **4** for **3c**.

water under the same amine concentration (Table 3). Irradi-ation by light of $\lambda > 400$ nm under air results in fast disappearance of **3a** and low yields of the amination prod-ucts for long-time irradiation. When the irradiation was car-ried out under nitrogen or with a light of $\lambda = 400$ nm, which is mainly absorbed by the acid form of **3a**, the lowering of the yield was considerably suppressed. As shown in Table 3, the yield of the amination products under air was nearly identical with that under nitrogen for relatively short-time irradiation in water–acetonitrile mixed solvents. Decompo-sition of **3a** via the excited base form in the presence of oxy-gen should be anticipated from these results. Anthraquinone derivatives having electron-donating substituents decompose in the presence of oxygen and hydroxide ion by visible light irradiation [32,33]. The same type of decomposition pre-sumably occurred via the dissociated form. As mentioned above, the efficiency of amination of **3c** was relatively low. The same type of decomposition might also be possible as one of reasons for the low efficiency because of higher degree of dissociation (0.4).

The reactivities of the leaving atom of the hydroxy-anthraquinones (**3b,c**) contrasted strikingly with those of the aminoanthraquinones (**2**). In the case of the aminoan-thraquinones, the bromine atom at position 4 was extremely more reactive than the hydrogen atom as predicted based
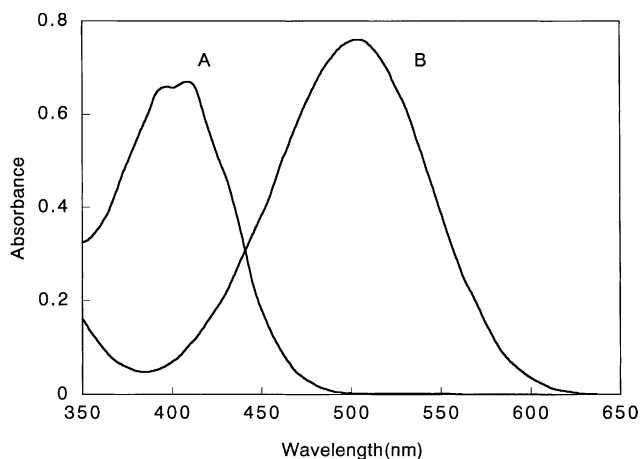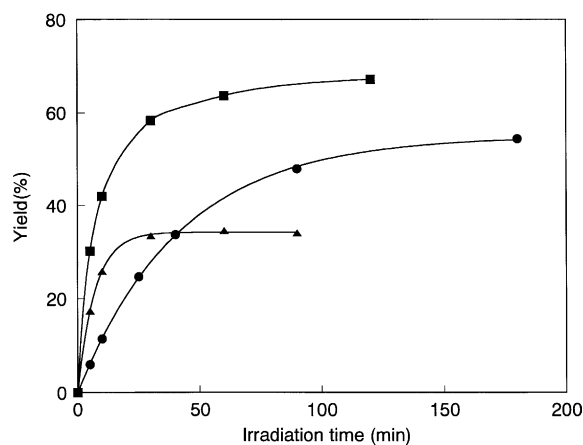

Fig. 1. Absorption spectra of 1-hydroxy-2-bromoanthraquinone (**3b**) in ethanol ([**3b**] = 9.76×10^{-5} mol dm^{-3}; A: acid form; B: base form).

Table 2
Relative reactivities at the 4-position of **1**, **2** and **3**[a,b]

	1a/1b	2a/2b	3b/3c
$\Phi(H)^c/\Phi(Br)^c$	0.14	0.012	7.7

[a] Solvent: acetonitrile.

[b] The concentration of *n*-butylamine and the excitation wavelength for each pair of the derivatives were as follows: **1a**, **1b**: 1.3 mol dm^{-3}, 400 nm; **2a**, **2b**: 1.0 mol dm^{-3}, 470 nm; **3b**, **3c**: 0.67 mol dm^{-3}, 470 nm.

[c] Quantum yield of the photoamination under air. Atom in parentheses is the leaving atom at the 4-position.

on the usual nucleophilic substitution mechanism (Table 2). On the other hand, the hydrogen atom at the 4-position of **3b** was anomalously more reactive than the bromine atom of **3c** (Table 2). This result is quite different from the photoamination of 1-aminoanthraquinones. The extraordinary characteristic of the hydroxyanthraquinones may suggest that a different mechanism operates for the photoamination of 1-hydroxyanthraquinones.

3.3. Production ratio in the photoamination of 1-hydroxyanthraquinone

Two products were formed in the photoamination of **3a** as mentioned in the previous section. Effects of solvent and of reaction atmosphere on the photoamination have been investigated to seek possible control of the product distribution and to obtain information regarding the reaction mechanism.

As mentioned above, **3a** at its ground state is in acid–base equilibrium in the presence of an amine. It is not clear whether the acid–base equilibrium is established in the excited state or not, but both dissociated (base) and undissociated (acid) forms of the hydroxyl group in **3a** should exist after the excitation of each of the two forms. Hence, both forms can participate in the reaction. The higher the water content of the solvent, the more easily is the hydroxyl group dissociates not only in the ground state but also in
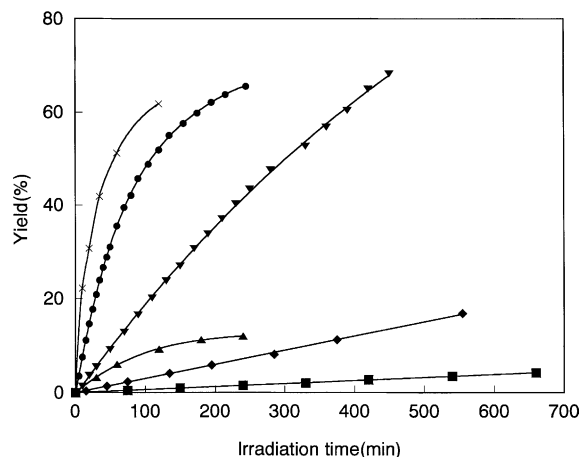

Fig. 3. Yield of **5 + 6** in the photoamination of **3a** under air in various solvents. [**3a**] = 3.0×10^{-4} mol dm^{-3}; [*n*-butylamine] = 5.0×10^{-2} mol dm^{-3}; excitation wavelength: 400 nm < λ < 430 nm; (●) acetonitrile; (■) benzene; (◆) *n*-hexane; (▲) methanol; (▼) isobutyronitrile; (×) DMSO.

the excited state. Therefore, the contribution of the base form to the reaction should become larger with an increase of water content. The change in the contributions of the base and acid forms to the reaction is expected to cause the change in the production ratio.

The ratios of quantum yield of **6**'s production to that of **5**'s in water–acetonitrile mixed solvents are shown in Table 3. The quantum yields became lower with the increase in water content of the solvent under both air and nitrogen. While the ratio under air was approximately constant regardless of the water content, that under nitrogen became higher with the increase in water content. The ratio in the reaction in acetonitrile containing 50% water, where the degree of dissociation was 0.87, was about 16 times larger than that in acetonitrile (Table 3). Relative increase of **6**'s quantum yield with the increase of water content under nitrogen suggests contribution of the base form to the reaction. Since the water content did not affect

Table 3
Relative quantum yields of the photoamination of **3a** and ratios of the quantum yield of **6**'s production ($\Phi(\mathbf{6})$) to that of **5**'s ($\Phi(\mathbf{5})$) in water–acetonitrile mixed solvent[a]

Water content, H$_2$O (vol.%)	0	10	30	50[b]
Degree of dissociation of the hydroxy group	∼0	0.05	0.39	0.87
Under air				
$\Phi(\mathbf{6})/\Phi(\mathbf{5})$	0.19	0.21	0.23	0.22
$(\Phi(5) + \Phi(6))_{rel}$[c]	0.48	0.24	0.15	0.16
Yield of **5 + 6** (%)	11	5.3	2.6	2.5
Under nitrogen				
$\Phi(\mathbf{6})/\Phi(\mathbf{5})$	0.20	0.75	1.8	3.2
$(\Phi(5) + \Phi(6))_{rel}$[c]	1.0	0.26	0.14	0.10
Yield of **5 + 6** (%)	23	6.1	2.7	1.5

[a] Excitation wavelength: 400 nm; irradiation time: 45 min; [**3a**] = 2.1×10^{-4} mol dm^{-3}; [butylamine] = 5×10^{-2} mol dm^{-3}.

[b] Because of the high degree of dissociation of the hydroxyl group, the base form of **3a** was mainly excited.

[c] Relative quantum yield of the photoamination of **3a**.

Table 4
Quantum yield of photoamination of **3a** under air in various solvents[a]

Solvent	Acetonitrile	Isobutyronitrile	Methanol	DMSO	n-hexane	Benzene
$\Phi(\mathbf{5})^{b}$ $(\times 10^{-3})$	6.8	1.5	1.7	16	0.69	0.031
$\Phi(\mathbf{6})^{b}$ $(\times 10^{-3})$	1.5	0.33	0.39	4.2	0.054	~0.0016
$\Phi(\mathbf{6})/\Phi(\mathbf{5})$	0.22	0.22	0.23	0.26	0.078	~0.05

[a] $[\mathbf{3a}] = 3.0 \times 10^{-4}$ mol dm^{-3}; [butylamine] $= 5.0 \times 10^{-2}$ mol dm^{-3}; excitation wavelength: 400 nm $< \lambda <$ 430 nm.
[b] Quantum yield of the production of the compound in parentheses.

the production ratio in the reaction under air, this may be qualitatively explained by the assumption that the reaction through the base form is quenched effectively by oxygen. This assumption could be supported by the fact that the production ratio in the case of the acid form excitation (in acetonitrile) under air was the same as that in the case of the base form excitation under air (in acetonitrile containing 30 vol.% water at $[\mathbf{3a}] = 9.2 \times 10^{-4}$ mol dm^{-3} and [butylamine] $= 5.0 \times 10^{-2}$ mol dm^{-3}, where the quantum yield of **5**'s production ($\Phi(\mathbf{5})$) and that of **6**'s ($\Phi(\mathbf{6})$) were 2.0×10^{-2} and 4.7×10^{-3}, respectively). Furthermore, the $\Phi(\mathbf{6})$ in the case of the base form excitation (in acetonitrile containing 30 vol.% water at $[\mathbf{3a}] = 9.2 \times 10^{-4}$ mol dm^{-3} and [butylamine] $= 5.0 \times 10^{-2}$ mol dm^{-3}) under nitrogen (1.4×10^{-2}) was larger than that of $\Phi(\mathbf{5})$ (8.3×10^{-3}). This result may be attributed to that **6** is more favorably produced by the reaction via the excited state of the base form than by that via the excited state of the acid form. On the other hand, the quantum yield of **5**'s production under air tended to be higher than that under nitrogen in water–acetonitrile mixed solvents. Although the contribution of both the acid form and the base form to the reaction is considered clear, the features of the reaction may not be so simple as tentatively presumed above.

Formation of reduced species was observed in the case of the reaction under nitrogen from the spectral change of the irradiated solutions by introducing air. The production of **3a**'s radical anion was at least presumed from the absorption in the long wavelength region ($\lambda < 650$ nm) of the irradiated solutions, which is characteristic of radical anions of anthraquinones. Furthermore, the absorption tended to increase with the increase in water content of the solvent. An inner filer effect by the reduced species could be responsible for the result that the quantum yield in the reaction under nitrogen was lower than that in the reaction under air (Table 3).

The yield of the photoamination of **3a** largely depended on solvent polarity as shown in Fig. 3. While the yields in polar solvents were relatively high, those in nonpolar solvents were very low. A comparison of reactivity by quantum yield is presented in Table 4. The relative distribution of **6** in nonpolar solvents was much lower than that in polar ones. These results may suggest that a different mechanism operates in nonpolar solvents. Yoshida et al. [34] have been reported that **1a** was regioselectively photoaminated at its 4-position in benzene and that the reaction in acetonitrile

gave byproducts. Their results could reflect the difference in reaction mechanism occurring in benzene and in acetonitrile. As mentioned above, reduced species detected in acetonitrile and in mixtures of water, and acetonitrile under nitrogen. Furthermore, the reaction in acetonitrile was suppressed by addition of radical scavengers. Since electron transfer from amine to quinones occurs easier in polar solvents than in nonpolar ones, these facts strongly suggest the participation of radical species in the reaction in polar solvents.

The elucidation of the reaction mechanism of photoamination is now in progress. Because the reaction in acetonitrile was retarded by the addition of a triplet quencher, the excited triplet state could participate in the reaction. A process could be presumed that an electron transfers from butylamine to the excited triplet state of hydroxyanthraquinones.

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