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The Nucleophilic Photo-substitution Reaction of Anthraquinone Derivatives. I. The Photo-amination of Sodium 1-Amino-4-bromoanthraquinone-2-sulfonate

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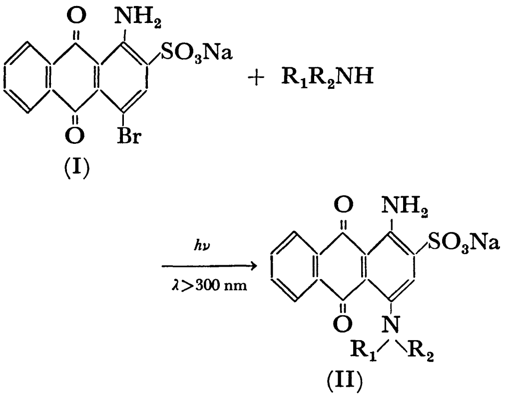
The photo-amination reaction of sodium 1-amino-4-bromoanthraquinone-2-sulfonate (I) was studied. The experimental results may be summarized as follows: 1) The photo-reaction is evoked by the absorption of light corresponding to the first absorption band (490 nm) of (I); 2) no dark reaction is observed: 3) aromatic amines appeared not to photo-react with (I); 4) the larger the polarity of the solvents used, the greater the yield of the product; 5) in the absence of oxygen, the photo-reaction was stopped. The possible reaction schemes were discussed.

The photochemistry of anthraquinone derivatives has attracted much attention in relation to the photo-tendering effects of vat dyes, and many studies concerning photo-reduction and photo-annelation have been reported.[1] However, the photo-substitution reactions of anthraquinones have rarely been reported on. Only two examples have been reported: the photolysis of 3-nitroalizarin in aerated methanol to give 4-methoxy-3-nitroalizarin, and the photolysis of anthraquinone-2-sulfonic acid in oxygen-free water to give hydroxyanthraquinones.[2,3] We ourselves have previously found that sodium 1-amino-4-bromoanthraquinone-2-sulfonate (bromamine acid) is photo-aminated to produce sodium 1,4-diaminoanthraquinone-2-sulfonate.[4] In this paper, details of the photo-amination will be reported and the most probable mechanism of the reaction will be discussed.



$R_1R_2NH \sim NH_3$, CH_3NH_2, $C_2H_5NH_2$, n-$C_3H_7NH_2$, n-$C_4H_9NH_2$, CH_2-$(CH_2)_4$-NH.

Experimental

Materials. The sodium 1-amino-4-bromoanthraquinone-2-sulfonate(bromamine acid) was purified by repeated salting out and by subsequent recrystalization from 1 : 1 ethanol-water. The sodium 1,4-diaminoanthraquinone-2-sulfonate was prepared by the hydrolysis of sodium 1-amino-

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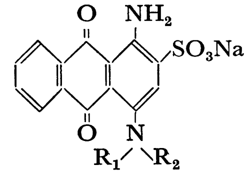
[1] J. M. Bruce, *Quart. Rev.*, **21**, 405 (1967).

[2] H. C. Van Beek and P. P. Heertjes, *J. Chem. Soc.*, **1962**, 83.

[3] A. D. Broadbent, *Chem. Commun.*, **1967**, 382.

[4] H. Inoue, T. D. Tuong, M. Hida, and T. Murata, *J. Chem. Soc., D*, **1971**, 1347.

TABLE 1. λ_{max} OF PHOTO-AMINATED PRODUCTS IN 4 : 1 2-PROPANOL–WATER

	$-N\langle^{R_1}_{R_2}$					
	$-NH_3$	$-NHCH_2$	$-NHC_2H_5$	$-NHC_3H_7$	$-NHC_4H_9$	$-N-(CH_2)_4-CH_2$
λ_{max} (nm)	565 607	588 634	587 633	586 632	587 633	605

4(N-benzenesulfonyl)-aminoanthraquinone-2-sulfonate. The other authentic samples of sodium 1-amino-4-alkylamino-anthraquinone-2-sulfonate were prepared in an autoclave by an Ullmann condensation reaction from bromamine acid and the corresponding alkylamine in the presence of cupric sulfate as the catalyst.

Solvents. Water was passed through ion-exchange resin columns (specific resistance: 10^6 ohm/cm). The methanol was purified by repeated fractional distillations. The 1-propanol and tertiary butanol were refluxed over lime and fractionally distilled. The ethanol was distilled with 5 ml of concd sulfuric acid and 20 ml of water per liter; then it was refluxed with silver nitrate and potassium hydroxide, and finally fractionally distilled. The acetonitrile was refluxed with sodium carbonate and potassium permanganate, and then distilled. It was subsequently refluxed with phosphorus pentoxide, fractionally distilled, and finally distilled over potassium carbonate. The extra-pure reagent of dioxane (Tokyo Kasei Co.) was used without further purification.

Measurements. A Shimadzu recording spectrophoto meter, model MPS 50, was used for the measurements of the visible absorption spectra.

Isolation of the Product. After the irradiation of light, the solvent was distilled from the reaction system at 30 °C under reduced pressure; the blue-colored product was separated by the method of cellulose-column chromatography with a developing solution of water.

Results and Discussion

Photo-reaction of I with Various Amines. A solution of 0.990×10^{-4} mol/l of bromamine acid and 4.37×10^{-2} mol/l of ammonia in an aerated 4 : 1 2-propanol–water mixture was irradiated at 30 °C by means of a water-jacketed 500 W high-pressure mercury lamp filtered with a glass which allows a radiation of $\lambda>300$ nm. The color of the solution turned from red to blue upon the irradiation. The visible absorption spectrum of the reaction system is shown in Fig. 1. As the reaction proceeded, the absorption intensity at 490 nm(λ_{max}) decreased with the increase in the intensities at 565 nm(λ_{max}) and 607 nm(λ_{max}), and the isosbestic points were at 382 nm and 525 nm. The newly-appeared absorption bands of 565 nm(λ_{max}) and 607 nm(λ_{max}) agreed with those of the authentic sodium 1,4-diaminoanthraquinone-2-sulfonate(II). Hence, this result suggested that the photo-reaction of bromamine acid(I) with ammonia gives only sodium 1,4-diaminoanthraquinone-2-sulfonate(II). The IR spectrum of the blue product and the paper chromatogram also supported this suggestion. Similar photo-aminations of bromamine acid(I) by alkylamines such as methylamine, ethylamine, *n*-propylamine, *n*-butylamine, and the piperidine were also observed. The wavelengths of the maximum absorption in the visible region of products in 4 : 1 2-propanol–water are compared in Table 1. In the case of piperidine, the reaction proceeds rather fast as compared with the case of other alkylamines. As is shown in Fig. 2, when the irradia-

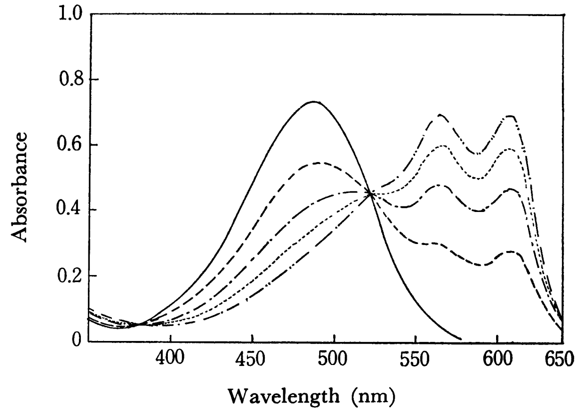


Fig. 1. Visible absorption spectra of the reaction system $[I]\sim0.990\times10^{-4}$ mol/l, $[NH_3]\sim4.37\times10^{-2}$ mol/l in 4 : 1 2-PrOH-H_2O.
——: 0 hr, ----: 2 hr, —·—: 4 hr, ······: 6 hr, —··—: 8 hr.

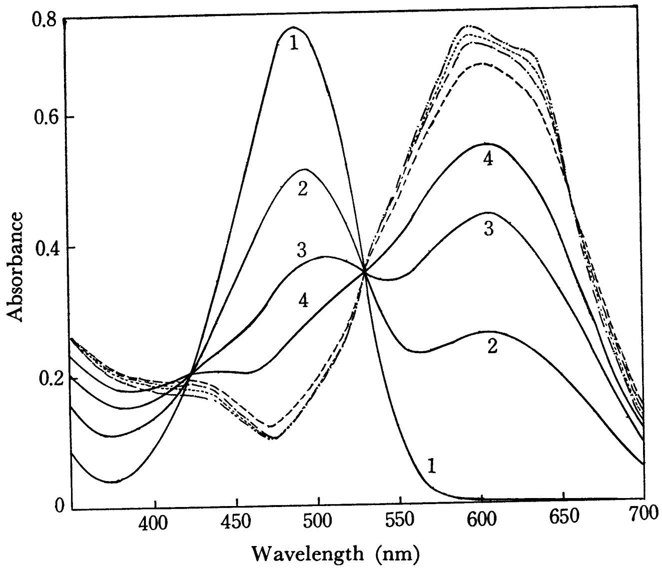


Fig. 2. Visible absorption spectra of the reaction system $[I]\sim0.990\times10^{-4}$ mol/l. $[Piperidine]\sim5.00\times10^{-2}$ mol/l in 4 : 1 2-PrOH-H_2O.
1: 0 min, 2: 20 min, 3: 40 min, 4: 60 min,
----: 2 hr, —·—: 4 hr, ----: 6 hr, —··—: 8 hr.

tion was carried out for more than 1 hr, the isosbestic point at 423 nm in the early stage of reaction disappeared and new two isosbestic points appeared in the neighbourhoods of 350 nm and 660 nm. Moreover, the broad absorption band of 605 nm(λ_{max}) split into two peaks; it resembles that in the spectrum of the reaction products of other alkylamines. These facts seem to indicate that bromamine acid may be photo-aminated by piperidine to produce sodium 1-amino-4-piperidinoanthraquinone-2-sulfonate, followed by the ring opening of the piperidine ring. When aromatic amines such as aniline and diphenylamine were used, the substitution reaction did not occur and (I) remained unchanged.

Photo-reaction of I with the Hydroxyl Ion. A solution of 0.990×10^{-4} mol/l of bromamine acid and 4.84×10^{-2} mol/l of sodium hydroxide in an aerated 4 : 1 2-propanol–water mixture was irradiated under the same conditions as have been given above. The absorption intensity of the first band($\lambda_{max}=490$ nm) of bromamine acid decreased, and a new absorption band at 612 nm initially appeared and then decreased with the irradiation; that is, the photo-decomposition of bromamine acid by the hydroxyl ion takes place exclusively. Nothing about the new absorption band at 612 nm was made clear. However, this band seems likely to be caused by either of two possible intermediates. One is a photo-reduced intermediate, since the new absorption band has a tendency to disappear upon the bubbling in of air. The other is sodium 1-amino-4-hydroxyanthraquinone-2-sulfonate, which may be considered to be once produced and then soon decomposed, since it has an absorption peak at 612 nm in an alkaline solution.

Photolysis of I. A solution of 0.990×10^{-4} mol/l of bromamine acid in a 4 : 1 2-propanol–water mixture was irradiated under the same conditions as in the case of the reaction with ammonia. After 8 hrs' irradiation, no change was observed in the absorption spectrum of the reaction system; that is, bromamine acid remained unchanged in the absence of amines or hydroxyl ion.

Effect of the Solvent. The photo-substitution reactions of bromamine acid (I) with ammonia were carried out in various solvents. As is shown in Fig. 3, the yields of the aminated product decreased in the following order: 4 : 1 CH_3CN–H_2O>4 : 1 2-PrOH–H_2O>4 : 1 EtOH–H_2O>4 : 1 MeOH–H_2O>4 : 1 1-PrOH–H_2O>4 : 1 *t*-BuOH–H_2O>4 : 1 Dioxane–H_2O>H_2O; that is, bromamine acid is more reactive in polar solvents, such as acetonitrile and alcohols, than in less polar solvents, such as dioxane, except in the case of water. This seems to imply the existence of a polar intermediate, which may be stabilized by the polar solvents.

Effect of the Wavelength of Irradiation. When the substance was irradiated with light including the UV region ($\lambda<300$ nm), the photo-amination reaction did not take place and the photo-decomposition of bromamine acid predominated. When the irradiating light was $\lambda>420$ nm, including only the region of the first absorption band ($\lambda_{max}=490$ nm), the substitution reaction proceeded as well as in the case of the radiation of $\lambda>300$ nm. Moreover, no dark reaction was observed under the same conditions in the case of any amine. From these results it may be concluded that the amination of bromamine acid by ammonia is induced by the absorption of light corresponding to the first absorption band of bromamine acid.

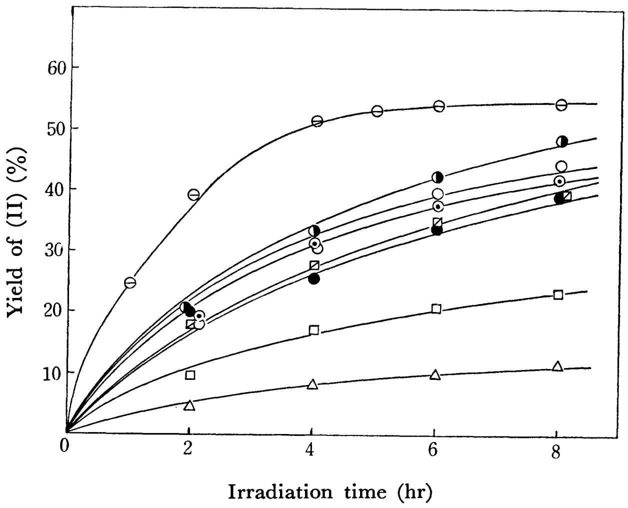


Fig. 3. Effect of the solvents on the yield of (II) [I]~0.990×10^{-4} mol/l, [NH_3]~4.37×10^{-2} mol/l.
⊖: 4 : 1 CH_3CN-H_2O, ◑: 4 : 1 2-PrOH-H_2O,
○: 4 : 1 EtOH-H_2O, ⊙: 4 : 1 MeOH-H_2O,
⧄: 4 : 1 1-PrOH-H_2O, ●: 4 : 1 *t*-BuOH-H_2O,
□: 4 : 1 Dioxane-H_2O, △: H_2O.

Photo-reaction of 1-Bromoanthraquinone with Ammonia. A solution of 1-bromoanthraquinone (1.0×10^{-4} mol/l) and ammonia (4.37×10^{-2} mol/l) in a 4 : 1 2-propanol–water mixture was irradiated in the way described above. No change was observed in the near UV and visible absorption spectra of the reaction system, and it was concluded that 1-bromoanthraquinone was not photoaminated by ammonia. This eliminates the possibility that the photo-induced cleavage of the C–Br bond may take place in the early stage of the photo-amination of bromamine acid.[5] This is also supported by the fact that no debrominated product such as sodium 1-aminoanthraquinone-2-sulfonate was detected in the photo-amination reaction of bromamine acid.

Effect of Oxygen. The reaction almost stopped under nitrogen. This suggests that dissolved oxygen has an important role in the photo-amination of bromamine acid. As has been mentioned above, the photo-reduction of quinones is well known, and the photo-amination may be considered to proceed through the intermediates which may be produced by several photo-

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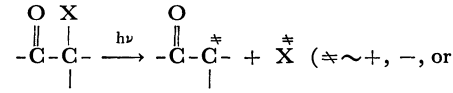
[5] Several examples of the photo-cleavage reactions of α-substituted aliphatic ketones, induced by the polarization of the C=O group in the excited n–π* state, are known to be;



$$-\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{\overset{X}{|}}{C}}- \xrightarrow{h\nu} -\overset{\overset{O}{\|}}{C}-\underset{|}{\overset{\mp}{C}}- + \overset{\mp}{X} \ (\mp\sim+, -, \text{or.})$$

where X is an electronegative species such as a halogen atom. (cf., for example, O. Jeger, K. Schaffner, and H. Wehrli, *Pure Appl. Chem.*, **9**, 555 (1964); J. A. Barltrop and A. Thomson, *J. Chem. Soc., C*, **1968**, 155; J. Hill, *Chem. Commun.*, **1966**, 260.)

reduction processes;[1,6,7]

a) $AQ^* + R\text{-}H \rightarrow AQH\cdot,\ AQH_2,\ AQ^{\overline{\cdot}}$

b) $AQ^* + OH^- \rightarrow AQ^{\overline{\cdot}}$

c) $AQ^* + R_1R_2\ddot{N}H \rightarrow [AQ^{\overline{\cdot}} \cdots\cdots R_1R_2\overset{+\cdot}{N}H]$

$$\begin{tikzcd} {[AQ^{\overline{\cdot}} \cdots\cdots R_1R_2\overset{+\cdot}{N}H]} \arrow[d] \\ AQ^{\overline{\cdot}},\ AQH\cdot \end{tikzcd}$$

However, in the presence of oxygen it is well known that these intermediates are immediately oxidized and that the quinone is regenerated.[8,9] In the case of sodium anthraquinone-2-sulfonate, Bridge and Reed observed that the concentrations of the intermediate semiquinone radical and the radical anion decrease with the increase in the oxygene concentration.[10] Therefore, if the photo-amination proceeds through these intermediates, the reaction is expected to be enhanced under nitrogen and retarded under air. However, the experimental results were contrary to the above expectation. Therefore, it seems that this scheme is also invalid. Further, Cooper and Talbot observed that both oxygen and metal ions, such as Fe^{3+}, have oxidizing power for intermediate radicals which are generated from quinones by photo-reduction.[11] According to their report, the photo-reaction of bromamine acid with ammonia in a 4 : 1 2-propanol–water mixture was carried out under nitrogen in the presence of Fe^{3+} (about 10^{-2} mol/l of ferric chloride or potassium ferricyanide) in place of the molecular oxygen. If the photo-amination reaction proceeds through the process of oxidation by the molecular oxygen of intermediate radicals generated in the photo-reduction of the anthraquinone nucleus, the reaction may be expected to take place upon the addition of Fe^{3+} as an oxidizing agent under nitrogen. However, no reaction was observed. These results suggest that molecular oxygen does not act as a simple oxidizing agent, but plays a more complicated role in the photo-amination reaction. The following other possible photochemical schemes including interactions with oxygen were also considered:

i) the photo-amination through the interaction of bromamine acid with singlet oxygen, which may be produced by the sensitizing effect of the triplet state of bromamine acid;

ii) the photo-amination through the interaction of excited bromamine acid with ground-state oxygen to form some complex as below:[12]

$$\begin{tikzcd} AQBr^* + O_2 \arrow[r] & {[AQBr^{\oplus} \cdots\cdots O_2^{\ominus}]} \arrow[dl] \arrow[dr, "R_1R_2NH"] & \\ AQBr + O_2 & & \text{Amination} \end{tikzcd}$$

etc.

It seems very difficult to deduce the mechanism of the photo-amination reaction of bromamine acid from only the above experimental results. A detailed kinetic study of the reaction will be reported in the near future.

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[6] In the study of the photo-reduction of 2-piperidinoanthraquinone, Phllips and his co-workers reported that, in a high concentration of the hydroxyl ion, the electron transfer from the hydroxyl ion to the excited 2-piperidinoanthraquinone can take place. (G. O. Phillips, A. K. Davies, and J. F. McKeller, *J. Chem. Soc.*, D, **1970**, 519).

[7] S. G. Cohen and A. D. Litt, *Tetrahedron Lett.*, **1970**, 837.

[8] J. L. Bolland and H. R. Cooper, *Nature*, **172**, 413 (1953).

[9] *Idem*, *Proc. Roy. Soc.*, *Ser.*, *A*, **225**, 405 (1954).

[10] N. K. Bridge and M. Reed, *Trans. Faraday Soc.*, **56**, 1796 (1960).

[11] H. R. Cooper and Miss B. M. Talbot, *ibid.*, **61**, 506 (1965).

[12] In the study of photo-fading of xanthene dyes complex formation between excited dye and ground state oxygen has been reported as,

$$D^*(T) + O_2 \longrightarrow [\overset{\oplus}{D}\cdots\overset{\ominus}{O_2}]$$

Y. Usui and M. Koizumi, This Bulletin, **40**, 440 (1967).