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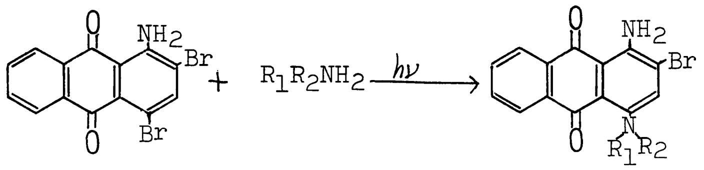
# NUCLEOPHILIC PHOTO-SUBSTITUTION REACTION OF ANTHRAQUINONE DERIVATIVES. III
# THE PHOTOAMINATION OF 1-AMINO-2,4-DIBROMOANTHRAQUINONE[1]

Haruo INOUE and Mitsuhiko HIDA
Department of Industrial Chemistry, Faculty of Engineering,
Tokyo Metropolitan University, Setagaya-ku,
Tokyo 158

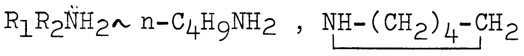
1-Amino-2,4-dibromoanthraquinone (I) was photoaminated by alkylamines with the irradiation of the light corresponding to the first absorption band of (I). The photoamination in benzene did not require oxygen and was quenched by anthracene, while the photoamination in acetonitrile did require oxygen and was not quenched by anthracene. Possible mechanism involving an inversion between $n\pi^*$ and $\pi\pi^*$ level was discussed.

The photochemical behavior of anthraquinone and it's derivatives with electron withdrawing substituents has been investigated intensively, and the lowest excited $n\pi^*$ triplet state is reactive in the photoreduction or the photosubstitution.[2~7] On the other hand, anthraquinone derivatives with electron donating substituents such as aminoanthraquinones have been generally known to be photochemically inactive because of their lowest excited states being intramolecular charge transfer states.[2,8] However, we observed that sodium 1-amino-4-bromoanthraquinone-2-sulfonate was photoaminated through an interaction between the lowest excited singlet c.t. state and the dissolved oxygen.[9,10] Recently the photoreduction of some of aminoanthraquinoes and methoxyanthraquinones and the photosubstitution of methoxyanthraquinones have also been reported.[11~13]

In this paper we will report on the photoamination of 1-amino-2,4-dibromoanthraquinone (1) and dramatic solvent effect on the photoamination suggesting a switch over of the reaction mechanism.



(I) (II)



$R_1R_2\ddot{N}H_2 \sim n\text{-}C_4H_9NH_2$ , $\underbrace{NH\text{-}(CH_2)_4\text{-}CH_2}$

Solution of (I) ($1\text{x}10^{-4}$ mol/l) and alkylamine (n-butylamine or piperidine) ($5\text{x}10^{-2}$ mol/l) in benzene was irradiated through a soda glass by a 500W Xe lamp (USHIO UXL-500D). The visible electronic absorption spectrum of the reaction mixture suggested that the aminated product (II) was produced effectively during the irradiation. Silica-gel thin layer chromatogram (mobile phase 93:7 benzene-acetone mixture), reversed phase paper chromatogram (stationary phase 1-bromonaphthalene, mobile phase 90% acetic acid saturated with 1-bromonaphthalene), and ir spectrum supported this suggestion. When the solution was irradiated by a monochromatic light of $\lambda$=470nm (fitered by Toshiba KL-47 and VY-45), the photoamination of (I) took place as effectively as in the case of the irradiation of $\lambda$>300nm. This indicated that the photoamination of (I) was induced by the absorption of the light corresponding to the first absorption band which has inherently the intramoleculer charge transfer nature.

Table. Solvent effect on the photoamination of (I)[a)]

| Solvent | Atmospher | |
|---|---|---|
| | Air | Nitrogen |
| Benzene | 25.0 | 41.7 |
| Acetonitrile | 33.3 | 5.1 |

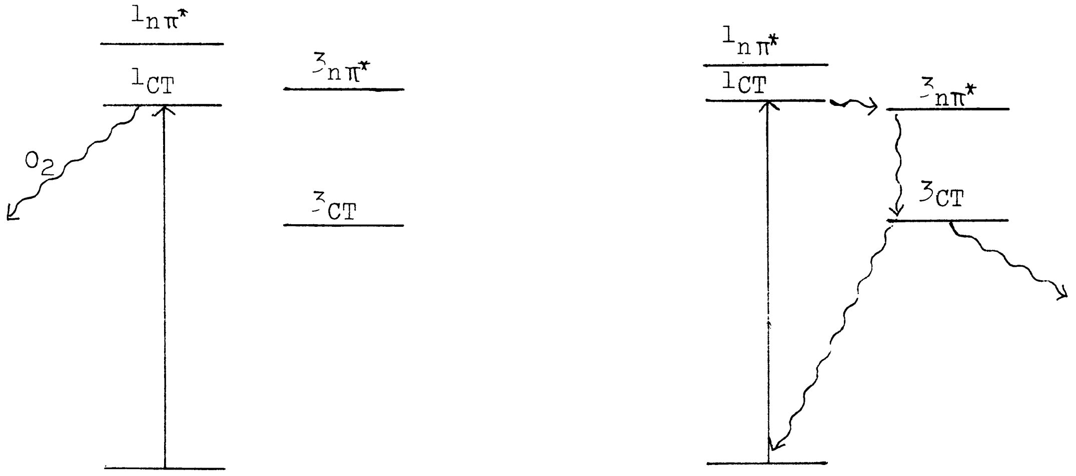
$[I] \sim 1.000\text{x}10^{-4}$ mol/l, $[n\text{-}C_4H_9NH_2] \sim 5.00\text{x}10^{-2}$ mol/l

$\lambda$>300nm, 5min. irradiation

a) Values in the arbitrary unit proportional to the yield of the aminated product (II)

As shown in Table, the photoamination of (I) in benzene was more reactive under nitrogen rather than under air saturation. The photoreaction in benzene was quenched considerably by the addition of anthracene as a triplet quencher ($E_T$=42 Kcal/mol) and sensitized by the addition of benzil ($E_T$=54 Kcal/mol) or fluorenone ($E_T$=53 Kcal/mol). On the contrary, the photoamination of (I) in acetonitrile strongly required the oxygen and did not be quenched by the addition of anthracene.

These striking contrast results suggest that 1) the reactive state of the photoamination of (I) in benzene is the lowest excited triplet c.t. state (between 54 Kcal/mol and 42 Kcal/mol) and the reactive state in acetonitrile is the lowest excited singlet c.t. state, and 2) the photoamination of (I) in benzene proceeds in a different manner from the photoamination in acetonitrile. The energy diagram of (I) in a polar solvent such as acetonitrile may be illustrated as Fig. a). The c.t. singlet state is considered to be a little lower than the $n\pi^*$ triplet state. Because of a low efficiency of the intersystem crossing between c.t. singlet and triplet states[14)], the photoamination of (I) proceeds mainly from the c.t. singlet by an interaction with oxygen as in the case of the photoamination of sodium 1-amino-4-bromoanthraquinone-2-sulphonate in a polar solvent.[9,10)] On the other hand, from a general consideration of the solvent effect on a $\pi\pi^*$ and a $n\pi^*$ level, it may be reasonably accepted that in a non-polar solvent such as benzene, the c.t. singlet is very much close to or a little higher than the $n\pi^*$ triplet as shown in Fig. b) resulting in the enhancement of the intersystem crossing to the c.t. triplet. Hence, the photoamination of (I) in benzene proceeds mainly from the c.t. triplet state with no interaction with oxygen. S.G.Cohen and his coworkers had observed similar solvent effect on the photoreduction of aminobenzophenones.[15)] Spectroscopic study is now being made to ensure above consideration.



a), in acetonitrile b), in benzene

Fig. Energy diagram of (I)

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