Photoinduced debenzylation of 2,5-bis(dibenzylamino)-3,6-dichloro-*p*-benzoquinone

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Abstract: In this detailed study of the photoreaction of 2,5-bis(dibenzylamino)-3,6-dichloro-*p*-benzoquinone, two new products were separated along with the previously reported debenzylated analogues, and their molecular structure was determined. One compound was identified as 2-(benzylamino)-3,6-dichloro-5-(dibenzylamino)-*p*-benzoquinone, which was found to undergo further debenzylation to form the two known debenzylated analogues. The

other compound was identified as the hydroquinone form of the starting material. This photoreaction was examined in detail using various analytical techniques under different experimental conditions, and a plausible reaction pathway was proposed on the basis of the experimental results. In addition, the reaction was found to occur also under sunlight irradiation.

1. Introduction

Organic dyes have attracted much attention as a new class of functional materials because they undergo changes in structure and properties when exposed to light, and their photoreactions offer potential applications in sensors, displays, and memory devices. Photochromic dyes are a typical example of light-functional dyes [1-11], which undergo structural changes upon photochemical reactions such as photoelimination, photocyclization, and photoisomerization. Photodegradation is a particularly important photoreaction of dyes. Specifically, organic colorants such as dyes and pigments tend to fade upon exposure to light. Despite the numerous reports on the light fastness of colorants from both scientific and industrial perspectives, a thorough understanding of this phenomenon is a challenging task [12-23].

We previously reported that the benzyl groups of 2,5-bis(dibenzylamino)-3,6-dichloro-*p*-benzoquinone (**1**) are easily eliminated under ambient light to give 2,5-bis(benzylamino)-3,6-dichloro-*p*-benzoquinone (**2**) and 2-amino-5-benzylamino-3,6-dichloro-*p*-benzoquinone (**3**)

(Scheme 1) [24].

  To our knowledge, it was the first report on the debenzylation of amino groups in organic dyes, whereas there are several reports on the corresponding *N*-dealkylation reaction [25-27]. Quinone derivatives are an important class of compounds for photosynthetic processes, and their characteristic response to light and energy-transfer properties have been extensively studied [28-37]. Moreover, they have been widely used as photoreactive materials for semiconductor manufacturing [38-42]. In contrast to these scientific and industrial applications of quinone derivatives, studies on the photoreactivity of aminobenzoquinones are limited, although several reports have been published on their photochemical cyclization [25, 43-46].

  The photoinduced *N*-debenzylation reaction could be applied to the synthesis of aminobenzoquinone derivatives under mild light conditions. Moreover, the eliminated species could serve as reactive species for further transformations under ambient light conditions [47-55].

  In this study, the experimental conditions of the photoinduced debenzylation of **1** were investigated in detail, and two new reaction products were identified. A possible mechanism is discussed, and the reaction was demonstrated to occur also under sunlight irradiation.

<Insert Scheme 1>

2. Experimental

2.1 Materials and instruments

All materials were used without further purification. Chloranil (95%) and dibenzylamine (97%) were purchased from Tokyo Chemical Industry Co., Ltd., and butylated hydroxytoluene (BHT) was purchased from Wako Pure Chemical Industries, Ltd. All solvents were obtained from Kanto Chemical Co., Inc. Column chromatography was performed on Wako silica gel C-300 (45-75 μm). Melting points were measured using a MEL-TEMP apparatus (Barnstead International Inc.). ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a DRX 300 Bruker spectrometer. UV-visible (UV-vis) absorption spectra were measured in solution with a Perkin Elmer Lambda 750 spectrometer. Infrared (IR) spectra were collected on a Perkin Elmer spectrum BX FT-IR system spectrophotometer. Elemental analyses (EA) of C, H, and N were performed with a CHNOS Elemental Analyzer Vario EL III (Elementar Co.). High-resolution mass spectrometry (HRMS) data were collected using a Jeol AccuTOF JMS-100LC (European Virtual Institute for Speciation Analysis) spectrometer. Electro-ionization mass spectrometry (EI-MS) spectra were measured with a JMS-600 mass spectrometer (JEOL Ltd.). Liquid chromatography-electrospray ionization mass spectrometry (LC-ESI-MS) spectra were recorded using a LaChrom Ultra-High Performance Liquid Chromatography system coupled to a time-of-flight mass spectrometer (Nano Frontier LD, Hitachi High-Technologies Co.). Photoirradiation was carried out using a Lightning cure spot light source LC8 (Xenon lamp, Hamamatsu Co.). The intensity of light irradiation was measured with a portable photoradiometer optical power meter V-550 (Newport Co.).

2.2 Irradiation experiment

The photoreaction of **1** was carried out under the same conditions and using the same equipment described in our previous report [24]. Moreover, the reaction was monitored by

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various spectroscopic techniques using the same parameters.

The photoreaction of **1** and newly identified intermediate **4** was monitored using UV-vis spectroscopy under the previously used irradiation conditions. The concentrations of the chloroform solutions of **1** and **4** were 1.0×10^{-2} mol dm^{-3} and 2.5×10^{-3} mol dm^{-3}, respectively. After a given time (10, 20, 30, 40, 60, 120, 180, 240, and 300 min for **1**, and 5, 10, 15, 20, 25, 30, 60, 120, 180, 240, and 300 min for **4**), 0.1 mL of the irradiated solutions was withdrawn, and the samples were kept in the dark until measurement. The concentrations of **1** and **4** were measured to be 1.67×10^{-4} mol dm^{-3} and 1.25×10^{-4} mol dm^{-3}, respectively.

The ^{1}H NMR spectral changes due to irradiation were investigated by analysing a sample of **1** before and after 300-min irradiation under room light (fluorescent lamp) at room temperature.

Monitoring by EI-MS and LC-ESI-MS was also performed under the same irradiation conditions. At time intervals of 30, 60, 180, and 300 min after starting the reaction, 2 μL of the reaction mixture was withdrawn and analysed after adjusting the concentration to 2.0×10^{-5} mol dm^{-3}. The LC-MS system was operated in positive ion mode, and the separation was carried out with a Poroshell 120 column (2.1×50 mm, 2.7 μm particle size, HPH-C18, Agilent Co., USA) using the following gradient system: 50% acetonitrile in water at 0 min; gradient to 90% acetonitrile at 8 min, and measurement until 15 min. The temperature of the column was kept at 30 °C. The photoreaction was also followed using a UV detector under identical conditions and set at 347 nm.

The reaction using sunlight as the light source was investigated. The experiment was carried out on a sunny day in the month of August 2016 between 9 AM and 2 PM in Yokohama City, Japan. The solar irradiance ranged from 0.15 to 0.22 W/cm^2 at 452 nm. During the photoreaction, the solution was stirred continuously with a magnetic stirrer under atmospheric

conditions.

2.3 Synthesis and characterization

2,5-Bis(dibenzylamino)-3,6-dichloro-*p*-benzoquinone (**1**) was synthesized by the reported procedure, and the chemical structure was confirmed by conventional analytical techniques [24].

2.3.1 Synthesis of aminobenzoquinones *4* and *5*

A chloroform solution of 2,5-bis(dibenzylamino)-3,6-dichloro-*p*-benzoquinone (**1**) (20 mL, 0.2 mmol) in a glass vial was irradiated with a Xe lamp under stirring at room temperature for 300 min. Then, the solvent was evaporated under reduced pressure, and the residue was purified by column chromatography using benzene as the eluent to obtain **4** and **5**. Previously reported debenzylated derivatives **2** and **3** were also obtained in 19% and 20% yield, respectively. The workup was carried out in the dark.

2-(Benzylamino)-3,6-dichloro-5-(dibenzylamino)-p-benzoquinone (4): green solid; yield: 52%; mp: 61-62 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 4.59 (s, 4H, CH$_2$), 5.00 (d, J = 6.0 Hz, 2H, CH$_2$), 6.45 (br s, 1H, NH), 7.14-7.19 (m, 4H, Ar-H), 7.27-7.38 (m, 11H, Ar-H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ (ppm) 175.0, 152.0, 142.3, 137.5, 137.1, 135.8, 129.0, 128.7, 128.1, 127.6, 125.5, 57.0, 48.7; IR (KBr pellet): *v* 3311, 3062, 3029, 2922, 1652, 1605, 1557, 1495, 1454, 1357, 1293, 1192, 742 cm^{-1}; HRMS: calcd for C$_{27}$H$_{22}$Cl$_2$N$_2$O$_2$Na ([M + Na]$^+$, based upon ^{35}Cl) 499.0096, found 499.0963; EA: Found: C 67.81%, H 5.00%, N 5.56%. Calc. for

$C_{27}H_{22}Cl_2N_2O_2$: C 67.93%, H 4.65%, N 5.87%; UV-vis (CHCl$_3$): λ_{max} 407 nm, ε 9.97 $\times$ 10^3 mol^{-1} dm^3 cm^{-1}.

2,5-Bis(dibenzylamino)-3,6-dichloro-p-hydroquinone (5): colourless solid; yield: 5%; mp: 147-149 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 4.21 (q, J = 6.0 Hz, 8H, CH$_2$), 7.11-7.14 (m, 8H, Ar-H), 7.25-7.28 (m, 12H, Ar-H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ (ppm) 156.6, 144.8, 137.6, 131.7, 129.2, 128.5, 127.7, 56.9; IR (KBr pellet): v 3250, 3027, 2890, 1495, 1450, 1423, 1380, 1190, 740 cm^{-1}; HRMS: calcd for $C_{34}H_{30}Cl_2N_2O_2Na$ ([M + Na]$^+$, based upon ^{35}Cl) 591.1582, found 591.1558; EA: Found: C 71.30%, H 5.39%, N 4.87%. Calc. for $C_{34}H_{30}Cl_2N_2O_2$: C 71.70%, H 5.31%, N 4.92%; UV-vis (CHCl$_3$): λ_{max} 314 nm, ε 1.50 $\times$ 10^5 mol^{-1} dm^3 cm^{-1}.

3. Results and discussion

3.1 Identification of photoproducts

We have previously reported that **1** is easily transformed into **2** and **3** upon irradiation by ambient light [24]. In those experiments, two byproducts were detected by thin-layer chromatography (TLC) during the reaction; however, their separation for characterization purposes was difficult. In the present study, the byproducts were successfully separated, and their chemical structures were determined. Yellow and colourless additional spots were observed on the TLC plate immediately after irradiation, and the spots corresponding to **2** and **3** appeared after 30 min. The yellow spot was relatively large whereas the colourless spot was very small. The product corresponding to the yellow spot readily converted into different compounds after separation; thus, the separation was carefully carried out in the dark, and the

yellow spot was identified as 2-(benzylamino)-3,6-dichloro-5-(dibenzylamino)-*p*-benzoquinone (**4**), derived from the removal of a benzyl group from **1** (Fig. 1 (a)). Various crystallization attempts of **4** by the solvent-diffusion method gave only amorphous green solids (Fig. S1). Moreover, we found that **4** could be transformed into **2** and **3** during crystallization, as also observed in the case of **1** [24].

The colourless TLC spot was also successfully separated and crystallized to obtain pale-yellow block crystals (Fig. S1). The molecular structure was determined by X-ray analysis [56] and conventional analytical techniques, and the compound was identified as 2,5-bis(dibenzylamino)-3,6-dichloro-*p*-hydroquinone (**5**), the hydroquinone form of **1** (Fig. 1 (b)).

<Insert Fig. 1>

*3.2 Photoreactivity of **4***

The brown colour of the chloroform solution of **4** faded under ambient light at room temperature with the concomitant appearance of new TLC spots corresponding to **2** and **3**. After several days under the same conditions, **2** and **3** were obtained in moderate yields. Shielding of light resulted in no colour change and no new TLC spots. The change in UV-vis absorption of a chloroform solution of **4** upon irradiation under the described conditions is illustrated in Fig 2 (a), and the inset graph shows the time-dependent change in absorption intensity at three specific wavelengths (322, 352, and 407 nm). The absorption maximum of **4** at 407 nm decreased rapidly, and a simultaneous increase in the intensity of the peak at 322 nm was observed. The latter peak was attributed to the hydroquinone form of **4**, although its

separation was not successful. After 60 min, the intensity of the peak at about 352 nm increased gradually. This peak corresponds to compounds **2** and **3**, which were obtained from **4** in 28% and 40% yield, respectively.

Next, the effect of light on the crystallization of **4** in chloroform and *n*-hexane was examined. Crystallization experiments of **4** without light-shielding resulted in the formation of red crystals of **2**, green crystals of **3**, and amorphous green solid **4** (Fig. S1). On the other hand, crystallization of **4** under light-shielding by aluminum foil successfully gave **4** as an amorphous solid.

3.3 Detailed examination of the photoreaction of 1

Detailed investigation of the photoreaction of **1** was performed by UV-vis, ^{1}H NMR, and mass techniques.

3.3.1 Monitoring by UV-vis spectroscopy

Fig. 2 (b) illustrates the UV-vis spectral changes of **1** in chloroform under irradiation for 300 min, and the inset graph shows the time-dependent changes at specific wavelengths (452, 352, 322, and 314 nm). As can be seen from the inset, the visible absorption of **1** at 452 nm rapidly decreased upon irradiation, and at the same time, the absorbances at 314 nm and 322 nm drastically increased at the beginning of the reaction. These bands were assigned to the hydroquinone forms of **1** and **4**, respectively. After about 60 min, these two components gradually decreased, and no drastic change was observed after 120 min. The intensity of the band at 352 nm, which originated from **2** and **3**, was found to increase at a constant rate after

30 min.

This result suggests that, in the first stage of the reaction, **1** was immediately converted into its hydroquinone form **5**, and the hydroquinone form of **4** was then generated. Further elimination of the benzyl groups gradually proceeded with conversion of hydroquinone to quinone to form **2** and **3** in the second step of the reaction. This reaction pathway was confirmed by other spectroscopic methods. We also carried out the reaction in benzene and toluene. The change in UV-vis absorption of a benzene solution of **1** upon irradiation is illustrated in Fig. S2. This result clearly indicated that the photoreactivity of **1** in benzene solution is almost similar to that in its chloroform solution. We also confirmed that this reaction occurred in toluene with the similar reaction behaviour. These results suggested that the possible proton source is water in solvent and/or air.

<Insert Fig. 2>

3.3.2 ^{1}H NMR spectral changes upon light irradiation

Fig. 3 shows the ^{1}H NMR spectra of **1** in CDCl$_3$ before and after 300-min irradiation. The colour of the solution gradually changed from brown to bright yellow during irradiation for 300 min. Before irradiation, only a singlet peak corresponding to eight protons was detected at 4.5 ppm, which was assigned to the four methylene groups (Fig. 3 (a)) and was useful for monitoring the chemical changes of **1** during the reaction. As can be seen from Fig. 3 (b), after irradiation, this peak was split into several components, and the aromatic multiplets at around 7-8 ppm indicated the presence of the hydroquinone form and debenzylated derivatives of **1**. A

hydroxyl and an amino proton peak at about 10 ppm and 6.3 ppm, respectively, were also observed.

This result suggests that, during the reaction, hydroquinone analogues of **1** were formed by the removal of one or more benzyl groups. The reaction process of **1** evidenced by ^{1}H NMR was in good agreement with that resulting from the UV-vis measurements.

In this experiment, we recognized a proton signal of the hydroxy group and the amino group of the derivatives under CDCl$_3$ solvent condition. This result supported our consideration on the proton source in this reaction described above.

<Insert Fig. 3>

3.3.3 Reaction monitoring by various chromatography - mass spectrometry techniques

Monitoring of the photoreaction of **1** by EI-MS showed that **4** appeared immediately after irradiation and its amount increased with time as the athmount of **1** decreased. After about 300 min, weak peaks corresponding to **2** and **3** were also observed. This led to the conclusion that **1** was converted into **4** in the first stage of the reaction, and then further transformed into **2** and **3**. This is in good agreement with the TLC and UV-vis results, although the possibility that the weak peaks of **2** and **3** derived from the fragmentation of **1** cannot be ruled out. In order to clarify this point, we attempted to monitor the reaction by LC-MS, and the results are shown in Fig. 4.

<Insert Fig. 4>

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In the mass spectrum of **1** before irradiation, the peaks of **1** and **5** were observed at a retention time (RT) of 9.4 min and 9.7 min, respectively. After 30 min, these peaks slightly decreased, and a peak with a RT of 6.5 min and a small peak at 7.8 min appeared. The first peak was assigned to the hydroquinone form of **4**, and the latter peak was assigned to **4**. The mass spectra, *m/z* values, and chemical structures corresponding to these signals are given in the Supporting Information (Fig. S3). At the last stage of the reaction, the intensity of the peaks of **1** and **5** significantly decreased, and that of the hydroquinone form of **4** increased. These results are consistent with those observed by UV-vis and ^{1}H NMR, i.e., **1** was rapidly converted into **5** and then into the hydroquinone form of **4**.

Even at a later stage, the peaks corresponding to **2** and **3** were not detected, presumably because of the positive ion measurement mode used in this study. The use of a mass spectrometer in positive or negative ion mode greatly affects the result obtained according to the charge of the target ions [57-59]. In this photoreaction, **2** and **3** react with the ions from the ion source of the mass spectrometer resulting in the removal of a hydrogen atom from Ar-NH and/or Ar-NH$_2$ groups to form negatively charged nitrogen atoms. This is a possible explanation for the lack of detection of **2** and **3** in the mass spectra recorded in positive mode.

Thus, we monitored the photoreaction of **1** by LC-MS analysis with UV detection (Fig. 4 (b)). In the first stage of the reaction, the absorption behaviour of **1**, **4**, and the corresponding hydroquinones was consistent with the LC-MS data. After 60-min irradiation, the absorption peaks of **2** and **3** were observed at RTs of 4.7 and 1.5 min, respectively. These two peaks rapidly increased with time, similarly to the spectral changes shown in Fig. 2. This result clearly indicates that the formation of **2** and **3** was difficult to detect by LC-MS.

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3.4 Effect of irradiation conditions

In order to better understand the photoreaction of **1**, the effects of nitrogen gas, irradiation time, and light intensity were investigated. We also carried out the reaction under sunlight irradiation.

\<Insert Table 1\>

Table 1 summarizes the yields of **2**, **3**, and **4** obtained under different experimental conditions and isolated by column chromatography. Halving the light intensity (0.3 W/cm^2) resulted in a slight increase in the yield of **4**, whereas the yields of both **2** and **3** were not significantly affected. In contrast, when the light intensity was increased 1.5 times (0.9 W/cm^2), the yield of **3** slightly increased. A similar result was obtained when the irradiation time was increased to 10 h. Thus, a strong light intensity and prolonged irradiation can result in a small increase in the yield of **3** with no significant changes in the yields of **2** and **4**. Performing the reaction under nitrogen made no significant difference, indicating that the debenzylation of **1** was not affected by the presence of oxygen.

Figure 5 shows the colour change of the reaction solution under sunlight irradiation. The colour change and TLC pattern were similar to those observed for the reaction performed with a Xe lamp as the light source. Moreover, the yields of **2**, **3**, and **4** were almost equivalent to those obtained from the reaction under Xe lamp irradiation.

Our findings revealed that the photoreactivity of **1** was not significantly affected by irradiation and atmospheric conditions. We also found that this reaction can proceed under sunlight irradiation.

<Insert Fig. 5>

3.5 Radical scavenging experiments

The photoreaction of benzoquinone derivatives has been reported to proceed via a radical mechanism [23-25, 31, 32]. Colourless and transparent, small benzoic acid crystals were observed during the crystallization of **1** (Fig. S4), which suggested that benzyl radicals were formed during the photoreaction of **1** [60-62]. Thus, in order to evaluate the involvement of a radical mechanism, the reaction was carried out in the presence of BHT as a radical scavenger. In particular, 20, 50, and 100 wt% of BHT were added to the reaction mixture, and the yields of **2**, **3**, and **4** obtained under these conditions and isolated by column chromatography are listed in Table 2. For the reaction in the presence of 50 wt% of BHT, the influence of nitrogen atmosphere was also examined.

<Insert Table 2>

The yields of **2** and **3** decreased considerably with increasing amount of BHT. In contrast, the amount of **4** was increased. As discussed in the previous sections, one benzyl group was

immediately lost from **1** at the beginning of the reaction, providing **4** mainly in the hydroquinone form. This result indicated that this step was not affected by BHT and therefore did not proceed via a radical mechanism. We also examined the reaction in the presence of BHT under nitrogen atmosphere. In the event, no remarkable difference was observed compared to the same reaction under atmospheric conditions, suggesting that the radical scavenging ability of BHT in this photoreaction was not significantly affected by oxygen.

Moreover, the colour change of the reaction solution was dramatically different in the presence of BHT (Fig. S5), and suggested that the photoreactivity of **1** decreased depending on the concentration of BHT. This is in line with the effect of BHT on the yield of the reaction products. After the radical scavenging reaction, the solution had a paler colour than after the reaction under normal conditions. This pale colour indicated a low concentration of **2** and **3** due to the suppression of benzyl group removal by BHT.

The radical scavenging experiments clearly demonstrated that photoelimination of benzyl groups from **4** to form **2** and **3** was effectively prevented by BHT whereas conversion of **1** into **5** and hydroquinone form of **4** was not significantly affected. We also confirmed that the radical scavenging activity of BHT in this photoreaction was not influenced by oxygen.

<Insert Table 2>

4. Conclusion

Two new products have been obtained and fully characterized from the photoreaction of 2,5-

bis(dibenzylamino)-3,6-dichloro-*p*-benzoquinone (**1**) along with the previously reported debenzylated analogues. One was identified as 2-(benzylamino)-3,6-dichloro-5-(dibenzylamino)-*p*-benzoquinone (**4**), which was found to convert into the two reported debenzylated derivatives (**2** and **3**). The other derivative was identified as the hydroquinone form of **1**, i.e., 2,5-bis(dibenzylamino)-3,6-dichloro-*p*-hydroquinone (**5**). The photoreaction was studied in detail using various analytical techniques under different experimental conditions. On the basis of the results, a plausible pathway was proposed (Scheme 2). In the first stage, compound **1** was rapidly transformed into the hydroquinone form **5**, which immediately underwent removal of a benzyl group to give compound **4** or its hydroquinone form. These were further transformed into debenzylated derivatives **2** and **3**. In this proposed mechanism, the detailed process of benzyl group removal has not been determined and needs to be further examined in the future. The second stage of the proposed pathway was demonstrated to be influenced by the presence of a radical scavenger. The photoreaction was also found to occur under sunlight irradiation.

Our findings will contribute to a deeper understanding of the photochemical reaction of aminobenzoquinones. In addition, this study shows the potential application of the reaction to a new synthesis of novel aminobenzoquinone derivatives under ambient light conditions. The electronic effect of the benzyl substituent and the photoreaction of dibenzylamino derivatives of other aromatic quinones will be investigated in a future study.

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