



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



In-Sub Shin^a, Yuta Shimada^a, Shinji Ishihara^b, Emi Horiguchi-Babamoto^c,
Shinya Matsumoto^{a,*}

^a Graduate School of Environment and Information Sciences, Yokohama National University, 79-7 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan

^b Instrumental Analysis Center, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501, Japan

^c Department of Pharmaceutical Sciences, Faculty of Pharmacy, Musashino University, 1-1-20 Shinmachi, Nishitokyo-shi, Tokyo, 202-8585, Japan

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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.

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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].

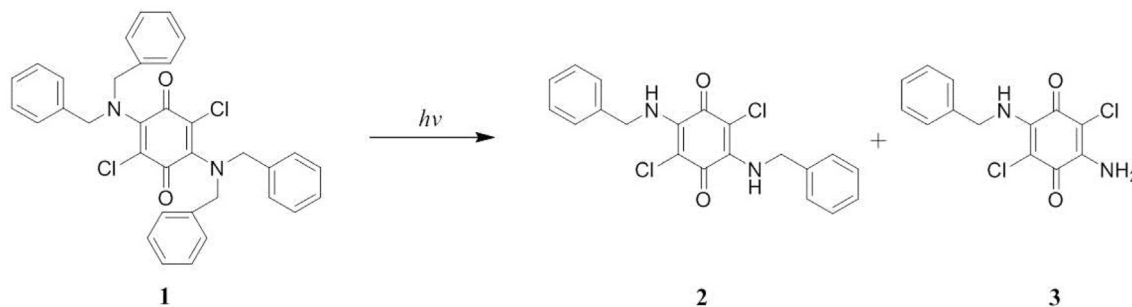
To our knowledge, it was the first report on the debenzylation of amino groups in organic dyes, whereas there are several reports on the corresponding *N*-dealkylation reaction [25–27]. Quinone derivatives are an important class of compounds for photosynthetic processes, and their characteristic response 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*-debzylolation 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,

* Corresponding author.

E-mail address: smatsu@ynu.ac.jp (S. Matsumoto).



Scheme 1. Photoreaction of aminobenzoquinone derivative **1**.

and the reaction was demonstrated to occur also under sunlight irradiation.

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 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 $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $2.5 \times 10^{-3} \text{ mol dm}^{-3}$, 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

$1.67 \times 10^{-4} \text{ mol dm}^{-3}$ and $1.25 \times 10^{-4} \text{ mol dm}^{-3}$, respectively.

The ^1H 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 $2.0 \times 10^{-5} \text{ mol dm}^{-3}$. The LC-MS system was operated in positive ion mode, and the separation was carried out with a Poroshell 120 column (2.1 \times 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 $^\circ\text{C}$. 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 a.m. and 2 p.m. 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 $^\circ\text{C}$; ^1H 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): ν 3311, 3062, 3029, 2922, 1652, 1605, 1557, 1495, 1454, 1357, 1293, 1192, 742 cm^{-1} ; HRMS: calcd for $\text{C}_{27}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2\text{Na}$ ($[\text{M} + \text{Na}]^+$, based upon ^{35}Cl) 499.0096, found 499.0963; EA: Found: C 67.81%, H 5.00%, N 5.56%. Calc. for $\text{C}_{27}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2$: C 67.93%, H 4.65%, N 5.87%; UV–vis (CHCl_3): λ_{max} 407 nm, ϵ $9.97 \times 10^3 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$.

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