

## Wavelength-dependent photolyses of 2,5-dichloro-3,6-bis(dialkylamino)-[1,4]benzoquinone

Min Shi<sup>\*</sup>, Wang-Gui Yang, Shuai Wu

East China University of Science and Technology, 130 Mei Long Lu, Shanghai 200237, China

Received 5 January 2006; received in revised form 26 May 2006; accepted 26 May 2006

Available online 3 July 2006

### Abstract

Photolysis of 2,5-dichloro-3,6-bis(dialkylamino)-[1,4]benzoquinone (**1**) at 254 nm or 300–500 nm produces the corresponding cyclized products (**2**) via the electron transfer-proton transfer sequence in a variety of solvents in quantitative yields within 10 min. In contrast, photolysis of 2,5-dichloro-3,6-bis(dialkylamino)-[1,4]benzoquinone (**1**) at >500 nm light source affords the elimination products (**3**) in good yields via the  $\delta$ -hydrogen abstraction.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Benzoquinone; Photolysis; Wavelength-dependent

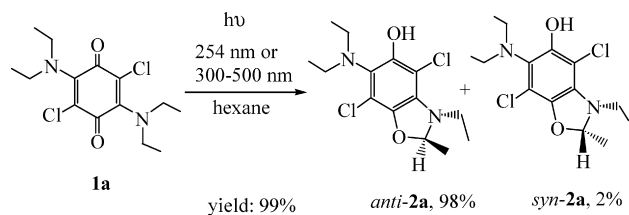
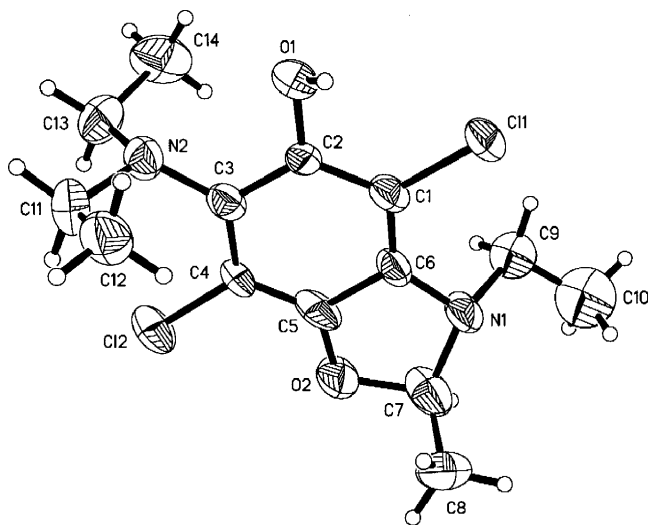
During the last several decades organic photochemistry has grown into an important and pervasive branch of chemistry [1]. Tremendous progress has been made in the theory of photochemical reactions, the utilization of photoreactions in synthetic sequences and the advancement of powerful laser techniques to study the mechanism of photoreactions [2]. Recently, the photoreaction of benzoquinone has attracted much attention [3]. In this paper, we report interesting photochemical behaviour of 2,5-dichloro-3,6-bis(dialkylamino)-[1,4]benzoquinone (**1**) upon irradiation at different wavelength. 2,5-Dichloro-3,6-bis(dialkylamino)-[1,4]benzoquinones (**1**) was synthesized by the reaction of 2,3,5,6-tetrachloro-[1,4]benzoquinone with the corresponding dialkylamine under mild conditions with an appropriate literature [4].

We found that upon photoirradiation of 2,5-dichloro-3,6-bis(diethylamino)-[1,4]benzoquinone (**1a**), a cyclized product (**2a**) was formed in quantitative yield as a mixture of *anti*- and *syn*-isomers (98:2) within short irradiation time (Scheme 1). Its structure was determined by spectroscopic data and X-ray diffraction. The ORTEP draw of *anti*-(**2a**) is shown in Fig. 1 [5]. The typical bond lengths and angles are shown in Table 1 and Table 2, respectively. The photolysis of (**1a**) also can be carried

out in a variety of solvents (3.0 mL) including dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), toluene, tetrahydrofuran (THF), ethyl acetate (EA), acetonitrile, and *N,N*-dimethylformamide (DMF) to produce the same product in similarly quantitative yields, although in polar solvents (acetonitrile,  $\text{CH}_2\text{Cl}_2$  or DMF), the photoreactions were relatively sluggish and 1 h was required for the completion of the reaction. It should be noted that photoirradiation with a 300 W high pressure mercury lamp through a glass filter of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (250 g/L) (365–500 nm) gave the similar results in a variety of solvents [6]. Thus, the cyclized product (**2a**) was formed upon irradiation with light source from 254 nm to 500 nm.

For the other 2,5-dichloro-3,6-bis(dialkylamino)-[1,4]benzoquinones (**1b**) and (**1c**), similar results were obtained under the above photoirradiation conditions. The results obtained upon irradiation of (**1**) in a Pyrex tube by a 300 W high pressure mercury lamp are summarized in Table 3. In all these cases, the corresponding cyclized products (**2**) are obtained in quantitative yields within 10 min, where *anti*-(**2**) was formed as the major product. In addition, in the photolysis of an oxygen-saturated hexane solution of (**1a**), the yield of (**2a**) was unchanged. On the basis of above results, a plausible reaction mechanism, involving a sequential electron transfer-proton transfer is shown in Scheme 2 [7]. The photo-excited state of (**1a**), probably in the singlet excited state, undergoes the intramolecular electron transfer to give radical ionic intermediate **A**. The proton transfer

<sup>\*</sup> Corresponding author. Tel.: +86 21 54925137; fax: +86 21 64166128.  
E-mail address: [mshi@pub.sioc.ac.cn](mailto:mshi@pub.sioc.ac.cn) (M. Shi).

Scheme 1. Photoirradiation of **1a** in hexane.Fig. 1. The ORTEP draw of *anti*-(**2a**).Table 1  
Typical bond lengths of *anti*-(**2a**)

Bond	Bond length (Å)
N(1)–C(6)	1.401
N(1)–C(7)	1.484
N(1)–C(9)	1.602
N(2)–C(3)	1.430
N(2)–C(13)	1.421
N(2)–C(11)	1.489
O(2)–C(5)	1.345
O(2)–C(7)	1.482

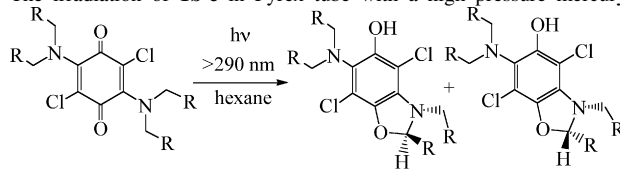
in **A** produces the biradical intermediate **B**, which undergoes the aromatization to give another biradical intermediate **C**. The cyclization of the resulting biradical intermediate **C** affords the corresponding product (**2a**). In order to clarify the reaction

Table 2  
Typical bond angles of *anti*-(**2a**)

Bond	Bond angle (deg)
C(6)–N(1)–C(9)	110.7
C(6)–N(1)–C(7)	106.1
C(7)–N(1)–C(9)	116.5
C(8)–C(7)–O(2)	107.8
C(8)–C(7)–N(1)	112.6
O(2)–C(7)–N(1)	105.0
C(5)–O(2)–C(7)	106.9
O(2)–C(5)–C(6)	111.3
O(2)–C(5)–C(4)	127.2
C(5)–C(6)–N(1)	108.1

Table 3

The irradiation of **1b–c** in Pyrex tube with a high pressure mercury lamp



**1b**: R = (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>      *anti*-**2b**: R = (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>      *syn*-**2b**: R = (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>  
**1c**: R = (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>      *anti*-**2c**: R = (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>      *syn*-**2c**: R = (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>

Entry <sup>a</sup>	Time (min)	Yield (%) <sup>b</sup> (2 ( <i>anti</i> : <i>syn</i> ))
1	10	<b>2b</b> , >99 (94:6)
2	10	<b>2c</b> , >99 (93:7)

<sup>a</sup> The similar results were obtained by irradiation with a glass filter of CuSO<sub>4</sub>·5H<sub>2</sub>O (250 g/L).

<sup>b</sup> Isolated yields.

mechanism, we added a radical inhibitor TEMPO (10 mol%) into the reaction solution. After the starting material **1a** was consumed (monitored by TLC), we found that the yield of **2a** decreased drastically, leading to the formation of **2a** in 45% yield. This result indicates that the reaction mechanism should be a radical process (Scheme 2). In this cyclization reaction, the *anti*-(**2a**) was formed as a major product presumably due to the steric hindrance of two alkyl groups.

Interestingly, when the irradiation of (**1**) was carried out by a light source having longer wavelength (>500 nm) (a infrared lamp), we found that the photoinduced elimination took place to produce the corresponding 2,5-dichloro-3-dialkylamino-6-ethylamino-[1,4]benzoquinone (**3**) in moderate to good yields in hexane [8]. The results are summarized in Table 4. Upon irradiation of (**1a–c**) at longer wavelength for 6 h, the corresponding products (**3a–c**) were obtained in 62–82% yields (Table 4, entries 1–3). The structures of 2,5-dichloro-3-dialkylamino-6-ethylamino-[1,4]benzoquinones (**3**) were determined by spectroscopic data, microanalysis, HRMS and X-ray diffraction. The ORTEP draw of (**3a**) is shown in Fig. 2 [9]. An intramolecular hydrogen bonding between N–H and carbonyl oxygen atom is seen (Fig. 2). The typical bond lengths and angles are shown in Table 5 and Table 6, respectively. The UV–vis spectra of (**1**) in various solvents revealed that a weak CT band exists from 500 nm to 600 nm. The UV–vis spectrum of (**1a**) in hexane is shown in Fig. 3. The CT band did not change at all

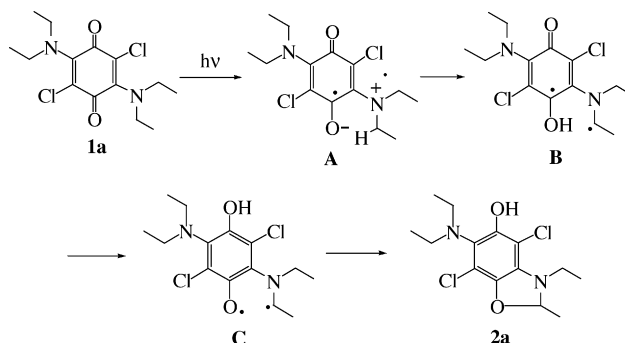
Scheme 2. A plausible reaction mechanism in the formation of **2a**.

Table 4  
Photoelimination of **1** by irradiation with daylight

**1a**: R = CH<sub>3</sub>  
**1b**: R = (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>  
**1c**: R = (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>

**3a**: R = CH<sub>3</sub>  
**3b**: R = (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>  
**3c**: R = (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>

Entry	Substrate	Solvent	Conv. (%)	Time (h)	Yield (%) <sup>a</sup>
1	<b>1a</b>	Hexane	90	6	<b>3a</b> , 82
2	<b>1b</b>	Hexane	76	6	<b>3b</b> , 67
3	<b>1c</b>	Hexane	75	6	<b>3c</b> , 62

<sup>a</sup> Isolated yields.

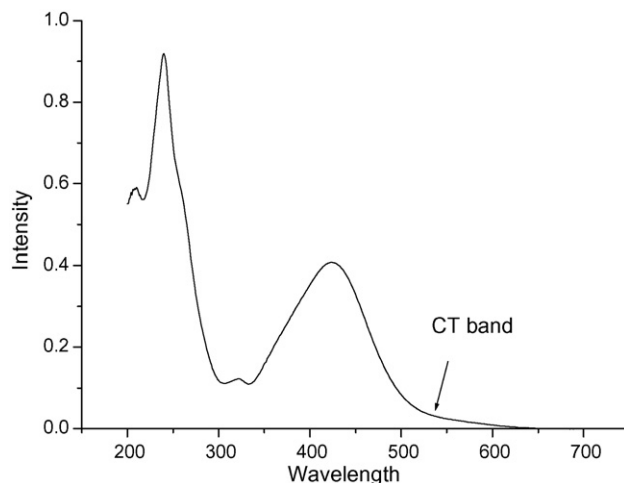


Fig. 3. UV-vis spectrum of (**1a**) (0.1 mM) in hexane.

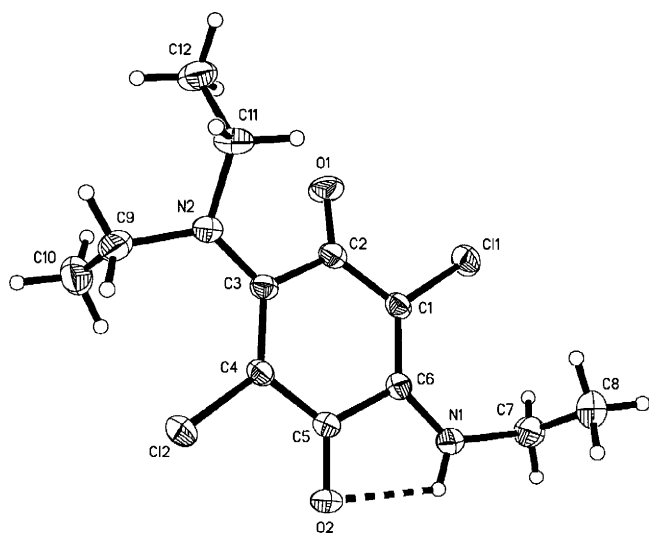


Fig. 2. The ORTEP draw of (**3a**).

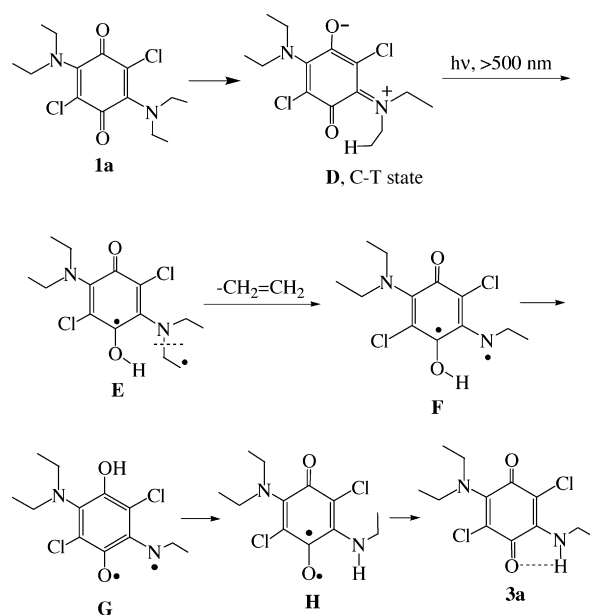
Table 5  
Typical bond lengths of (**3a**)

Bond	Bond length (Å)
N(1)–C(6)	1.325
N(1)–C(7)	1.460
N(2)–C(3)	1.343
N(2)–C(9)	1.469
N(2)–C(11)	1.481
O(2)–C(5)	1.233
O(1)–C(2)	1.219

Table 6  
Typical bond angles of (**3a**)

Bond	Bond angle (deg)
C(6)–N(1)–C(7)	130.1
C(5)–C(6)–N(1)	111.7
O(2)–C(5)–C(6)	117.4
O(2)–C(5)–C(4)	122.0
C(3)–N(2)–C(9)	121.8
C(3)–N(2)–C(11)	112.8

with the concentration of (**1a**) in hexane, which suggests that it should be an intramolecular CT band. On the basis of this observation, a plausible reaction mechanism that involves the  $\delta$ -hydrogen abstraction is shown in Scheme 3. The excitation of the weak intramolecular CT band of intermediate **D** in the visible region gives the biradical intermediate **E** via a  $\delta$ -hydrogen abstraction, which undergoes cleavage to give the biradical intermediate **F** along with the elimination of one ethylene molecule. The aromatization of **F** gives another biradical intermediate **G**. The proton transfer in biradical intermediate **G** produces the corresponding product (**3a**) presumably via the intermediate **H**. For [1,4]benzoquinones (**3b**) and (**3c**), the corresponding elimination products 1-butene and 1-hexene, 1-hexanal were detected by GLC and GC–MS analysis (Supporting Information) [10].



Scheme 3. A plausible reaction mechanism in the formation of **3a**.

The origin of this interesting reactivity change is not clear at present stage, but we believe that the  $\gamma$ -hydrogen is a bit far from the carbonyl oxygen in the intramolecular CT state with a more rigid aza-ortho-quinid structure, thus facilitating the abstraction of  $\delta$ -hydrogen.

In conclusion, we have found an interesting photo-induced reaction of 2,5-dichloro-3,6-bis(dialkylamino)-[1,4]benzoquinones (**1**). The wavelength of light source plays a significant role in determining the fate of photoexcited (**1**). Efforts are in progress to elucidate the mechanistic details of this reaction and to disclose its scope and limitations.

### Acknowledgments

We thank the State Key Project of Basic Research (Project 973) (No. G2000048007), Shanghai Municipal Committee of Science and Technology, East China University of Science and Technology of Changjiang Scholarship, and the National Natural Science Foundation of China (20472096, 203900502, and 20272069) for financial support.

### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.05.019.

### References

- [1] (a) J.J. McCullough, *Chem. Rev.* 87 (1987) 811–860;  
(b) G.J. Kavarnos, N.J. Turro, *Chem. Rev.* 86 (1986) 401–449;  
(c) W. Horspool, F. Lenci, *CRC Handbook of Organic Photochemistry and Photobiology*, second ed., 2004.
- [2] (a) R.R. da Silva, V.G. Toscano, R.G. Weiss, *Chem. Commun.* (1973) 567–568;  
(b) D.H.R. Barton, T.J. Bentley, R.H. Hesse, F. Mutterer, M.M. Pechet, *Chem. Commun.* (1971) 912–913.
- [3] (a) P. Boule, K. Othmen, C. Richard, B. Szczepanik, G. Grabner, *Int. J. Photoenergy* 1 (1999) 49–54;  
(b) D.W. Bahnemann, *Res. Chem. Intermed.* 26 (2000) 207–220.
- [4] (a) B.M. Awad, N.I.A. Sayed, E.M. Nassar, *Egypt. J. Chem.* 43 (2000) 467–482;  
(b) M. Alnabari, S. Bittner, *Synthesis* (2000) 1087–1090.
- [5] The crystal data of anti-(**2a**) has been deposited in CCDC with number 267271. Empirical formula:  $C_{14}H_{20}N_2O_2Cl_2$ ; formula weight: 319.22; crystal color, habit: colorless, prismatic; crystal dimensions: 0.53 mm  $\times$  0.47 mm  $\times$  0.41 mm; crystal system: orthorhombic; lattice type: primitive; lattice parameters:  $a = 10.015(3) \text{ \AA}$ ,  $b = 12.310(3) \text{ \AA}$ ,  $c = 26.483(7) \text{ \AA}$ ,  $V = 3264.9(14) \text{ \AA}^3$ ; space group: Pca2(1);  $Z = 8$ ;  $D_{\text{calc}} = 1.299 \text{ g/cm}^3$ ;  $F_{000} = 1344$ ; diffractometer: Rigaku AFC7R; residuals: R; Rw: 0.1099, 0.2658.
- [6] M. Kasha, *J. Opt. Soc. Am.* 38 (1948) 929–934.
- [7] For recent photochemical reaction of benzoquinone derivatives:  
(a) H.J.P. de Lijser, N.A. Rangel, *J. Org. Chem.* 69 (2004) 8315–8322;  
(b) A. Pochon, P.P. Vaughan, D. Gan, P. Vath, N.V. Blough, D.E. Falvey, *J. Phys. Chem. A* 106 (2002) 2889–2894;  
(c) G. Balakrishnan, P. Mohandas, S. Umopathy, *J. Phys. Chem. A* 105 (2001) 7778–7789;  
(d) H. Görner, *J. Phys. Chem. A* 107 (2003) 11587–11595;  
(e) M.K. Kadirov, S.E. Nefed'ev, M.B. Zuev, *Russ. Chem. Bull. Int. Ed.* 52 (2003) 905–909;  
(f) Y. Chen, M.G. Steinmetz, *Org. Lett.* 7 (2005) 3729–3732;  
For related reaction:  
(g) J.-P. Pete, R. Mortezaei, F. Henin, J. Muzart, O. Piva, *Pure Appl. Chem.* 58 (1986) 1257–1260;  
(h) O. Piva, R. Mortezaei, F. Henin, J. Muzart, J.-P. Pete, *J. Am. Chem. Soc.* 112 (1990) 9263–9272.
- [8] F. Henin, J. Muzart, J.-P. Pete, A. M'boungou-M'passi, H. Rau, *Angew. Chem.* 103 (1991) 460–462;  
F. Henin, J. Muzart, J.-P. Pete, A. M'boungou-M'passi, H. Rau, *Angew. Chem. Int. Ed. Engl.* 30 (1991) 416–418.
- [9] The crystal data of (**3a**) has been deposited in CCDC with number 267272. Empirical formula:  $C_{12}H_{16}N_2O_2Cl_2$ ; formula weight: 291.17; crystal color, habit: colorless, prismatic; crystal dimensions: 0.511 mm  $\times$  0.348 mm  $\times$  0.032 mm; crystal system: triclinic; lattice type: primitive; lattice parameters:  $a = 5.0263(8) \text{ \AA}$ ,  $b = 7.9682(12) \text{ \AA}$ ,  $c = 16.768(3) \text{ \AA}$ ,  $\alpha = 91.364(3)^\circ$ ,  $\beta = 94.230(3)^\circ$ ,  $\gamma = 92.226(3)^\circ$ ,  $V = 668.98(18) \text{ \AA}^3$ ; space group: P-1;  $Z = 2$ ;  $D_{\text{calc}} = 1.445 \text{ g/cm}^3$ ;  $F_{000} = 304$ ; diffractometer: Rigaku AFC7R; residuals: R; Rw: 0.0499, 0.1225. SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) are used to solve the structure.
- [10] Photo-induced rearrangement of chlorodialkylamino-1,4-benzoquinones into benzo[2,1-*d*]-2,3-dihydrooxazoles has been reported:  
A. Juodyiris, E.P. Fokin, *Izv. Sib. Otd. Akad. Nauk sssr, Ser. Khim. Nauk* (1970) 124–128.