Photoisomerization of Bromonaphthoquinone-fused Diphenylcyclopropane into Xanthylium Salt in the Presence of Arene Donors

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Irradiation of bromonaphthoquinone-fused diphenylcyclopropane in the presence of naphthalene, dimethoxybenzene or triphenylamine gave xanthylium salt *via* an intramolecular cyclization of intermediary 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone.

Photoinduced electron transfer (PET) is a useful and versatile means to promote chemical reactions between thermally stable electron donor and acceptor molecules, since the generated radical ions behave as reactive intermediates.[1] Our interest in the chemistry of quinone-fused cyclopropanes prompted us to apply the PET reaction to this strained ring system with a strong electron-acceptor component. Recently we found that the irradiation (>330 nm) of the title quinone-fused diphenylcyclopropane **1a** in the presence of alkyl amine donors provides the dimeric product **2** and the hydrogen bromide salts of amines *via* a reaction sequence involving a single electron transfer from the amine to the excited **1a**, a cyclopropane ring-opening associated with loss of Br$^-$, a collapse of the generated allyl radical **II** to the dimer **2**, and a proton donation of the amine cation radical to Br$^-$, giving HBr (isolated as amine salts)[2] (Scheme 1).

We wish to report here that this photochemical reaction was dramatically changed to furnish xanthylium salt when the proton trap of Br$^-$ is inhibited by use of arene donors (Scheme 1).

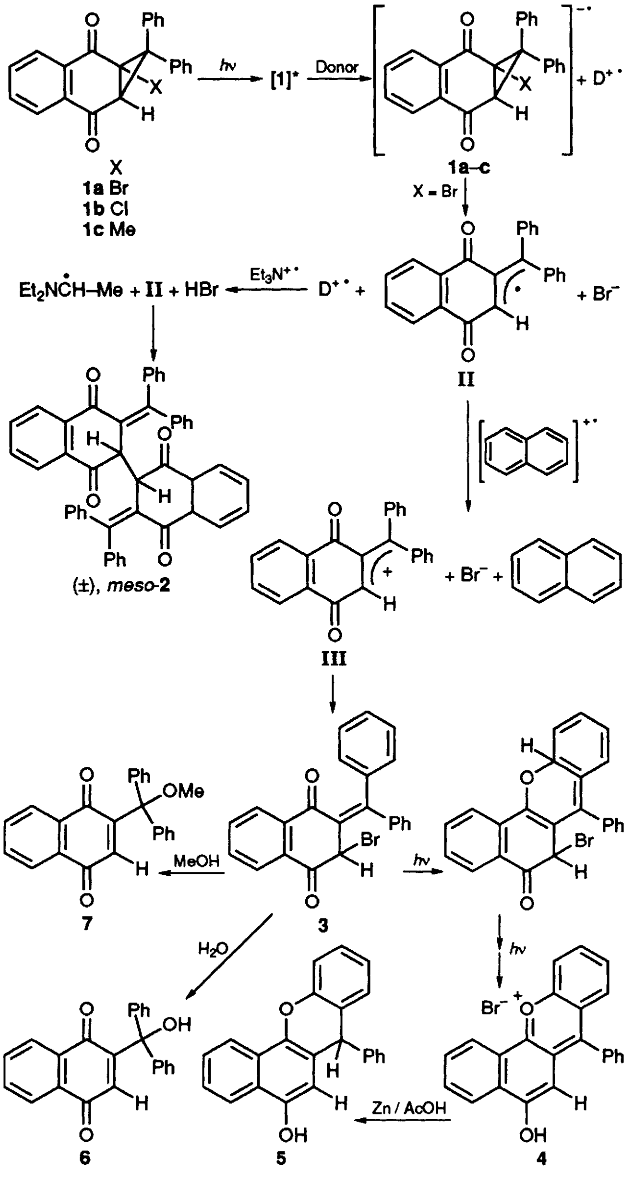
Photoreaction of cyclopropane **1a** (6.2 mmol dm^{-3}) and an equimolar amount of naphthalene, dimethoxybenzene or triphenylamine in acetonitrile afforded 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone **3**[†] and 5-hydroxy-7-phenyl-benzo[*c*]xanthylium bromide **4**.[‡] The structure of **4** was elucidated by the usual spectroscopic techniques as well as by chemical conversion into 5-hydroxy-7-phenylbenzo[*c*]xanthene **5**[§] (74.6%) on treatment with zinc powder in acetic acid.[3]

The general preparative procedure is described for the case of **1a** (50.0 mg) and *p*-dimethoxybenzene (17.1 mg) in acetonitrile. After irradiation, the solvent was evaporated and the reaction mixture was submitted to ^{1}H NMR analysis to determine the yield of product **3** by using an internal standard. The reaction mixture was washed with benzene (5 ml × 4) to separate insoluble xanthylium salt **4** (6 mg, 54.5% based on consumed **1a**). The combined washing solution was condensed and chromatographed on silica gel to give successively dimethoxybenzene (15 mg), unconsumed **1a** (39 mg, 78%), and 2-(α-hydroxy)diphenylmethyl-1,4-naphthoquinone **6** (1 mg, 10.8%) with increasing amount of benzene (≈100% by volume) in hexane. Compound **6** was derived from hydrolysis of **3** as a result of column chromatography. It is noted here that addition of methanol considerably delayed the conversion of **1a**[¶] and **3** reacted with methanol by an S_N' process to give 2-(α-methoxy)diphenylmethylnaphthoquinone **7** (entries 2 and 9).

The photochemical reaction did not occur in nonpolar solvents such as benzene or dichloromethane (entries 3 and 4). Use of chloro- or methyl-naphthoquinone cyclopropane derivatives **1b, c** also resulted in no reaction, with quantitative recovery of the cyclopropanes (entries 10 and 11). The product distributions and the reaction conditions are summarized in Table 1.

The fluorescence of **1a** was quenched by naphthalene and Stern–Volmer plots of fluorescence quenching *vs.* naphthalene concentration were linear, indicating electron transfer to the singlet excited state of **1a**. No new emission ascribable to exciplex fluorescence was observed in the quenching experiments. The value of the free energy change (ΔG) calculated according to the Weller equation for the system **1a**–naphthalene was negative $(-108$ kJ mol$^{-1})$. This is consistent with spontaneous electron transfer from naphthalene to the excited **1a**. No charge transfer absorption in acetonitrile appeared in a mixture of **1a** and an equimolar amount of naphthalene.

From these facts, we propose a possible mechanism of photoisomerization as given in Scheme 1. The first step is photoexcitation of **1** followed by single electron transfer from the donor to the excited singlet state of **1**. The radical anion **Ia** (X = Br) undergoes ring opening with loss of Br$^-$ to generate allyl radical **II**. Such Br$^-$ release will be suppressed in



Scheme 1

Table 1 Photoreaction of diphenylcyclopropanes **1a–c** with arene donors[a]

					Yield[c] (%)		
Entry	Cyclopropane	Donor	Solvent	Conversion[b] (%)	**3**[b]	**4**[e]	**7**
1	**1a**	Naphthalene	MeCN	13.7	9.5	60.6	—
2	**1a**	Naphthalene	MeCN-MeOH (90 : 10)[d]	5.6	0	35.7	49.5
3	**1a**	Naphthalene	C_6H_6	0	0	0	—
4	**1a**	Naphthalene	CH_2Cl_2	0	0	0	—
5	**1a**	*p*-Dimethoxybenzene	MeCN	22.0[f]	12.5	60.9	—
6	**1a**	*m*-Dimethoxybenzene	MeCN	12.0[f]	10.3	46.0	—
7	**1a**	*o*-Dimethoxybenzene	MeCN	13.8	10.8	63.0	—
8	**1a**	Triphenylamine	MeCN	48.5	4.8	69.5	—
9	**1a**	Triphenylamine	MeCN-MeOH (90 : 10)[d]	19.5	0	35.3	64.0
10	**1b**	Naphthalene	MeCN	0	0	0	—
11	**1c**	Naphthalene	MeCN	0	0	0	—

[a] Irradiation time 2h. [b] Unless otherwise noted, measured from NMR peak areas of the methine protons of remaining **1** and **3** with respect to the methylene peak area of 4-chloromethylbiphenyl used as an internal standard. [c] Based on consumed **1**. [d] By volume. [e] Determined by the UV absorption of **4** at λ_{max} = 532.2 nm [log(ε/dm^3 mol^{-1} cm^{-1}) = 3.70]. [f] Isolated yield.

nonpolar solvents. The next step is a back electron transfer from **II** to the radical cation of the donor giving the allyl cation **III**. The allyl cation recombines with the extruded Br$^-$ to yield **3**. For the unreactive **1b,c**, the radical anions **Ib,c** (X = Cl, Me) will simply transfer the electron to the counter radical cation of the donor as a consequence of the insusceptibility or poor lability of the substituent X. Formation of **4** may be rationalized by the photochemical 6π-electrocyclization of **3** and the electron reorganization accompanied by proton migration and Br$^-$ release, as judged from the appreciable decrease of **4** obtained owing to the competitive methanolysis of **3** (entries 2 and 9). In fact, direct irradiation of **3** in acetonitrile gave **4** in good yield (82.2%).

It is of much interest that similar photoreaction of **1a** in the presence of xanthene donor gave both the dimer **2** [(±), 5.4%; *meso*, 3.6%) and xanthylium **4** (38.7%) together with **3** (10.9%) and 9,9′-bixanthenyl (15.9%). This fact indicates that xanthene occupies a borderline position in the present dual photolytic processes on account of its increased proton donating ability relative to naphthalene.

In summary, it may be concluded that the cyclopropane **1a** undergoes photoinduced degradation, the pathway of which markedly depends on the nature of donor molecules, *i.e.* their proton donating ability. The nature of products obtained differs for NEt$_3$ and naphthalene, the radical of the former acts a proton donor (to Br$^-$) whilst the naphthalene radical cation undergoes SET with the allyl radical **II** (Scheme 1). A back electron transfer is also far more favourable for naphthalene than for Et$_3$N because of its higher ionization potential (1.60 *vs*. 0.76 eV).

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Footnotes

† The structure of **3** was confirmed by X-ray crystal structure analysis. Full details will be described elsewhere.

‡ The absorption spectrum of **4** recorded in acetonitrile was characterized by several strong absorptions with λ_{max} = 240.4 nm [log(ε/dm^3 mol^{-1} cm^{-1}) = 4.47], 315.3 (4.26), 395.0 (3.94), and 532.2 (3.70). IR spectra revealed no carbonyl absorptions. Mass spectrum by electrospray method showed one peak [*m/z* 323 (M − Br)]. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.71–8.45 (m, 12H), 8.64–8.68 (d, *J* = 9.91 Hz, 1H), 9.13–9.15 (d, *J* = 8.58, 1H Hz), 11.65 (s, 1H).

§ *Spectroscopic data* for **5**: mp 161–162 °C; ^{1}H NMR (CDCl$_3$): δ 5.00 (S, 1H), 5.27 (s, 1H), 6.40 (s, 1H), 6.94–7.08 (m, 2H), 7.15–7.30 (m, 7H), 7.46–7.64 (m, 2H), 8.06–8.09 (d, 1H, *J* = 7.92 Hz), 8.41–8.44 (d, 1H, *J* = 7.92 Hz); *m/z* 324 (M$^+$); satisfactory elemental analysis was obtained. Other new products also provided satisfactory analytical and spectroscopic data.

¶ The suppression of the conversion of **1a** by addition of methanol may be due to hydrogen bonding to **1a** and/or **1a*** by which the excitation of **1a** will be disturbed[4] and thermal decay of **1a*** will be more accelerated.

References

1 *Photo-induced Electron Transfer*, ed. M. A. Fox and M. Chanon, Elsevier, Amsterdam, 1988; K. Mizuno, N. Ichinose and Y. Otsuji, *J. Org. Chem.*, 1992, **57**, 1855; H. Tomioka and M. Kanda, *Chem. Lett.*, 1990, 2223.

2 H. Moriwaki, T. Oshima and T. Nagai, *J. Chem. Soc., Chem. Commun.*, 1994, 255.

3 W. Dilthey and H. Stephan, *J. Prakt Chem.*, 1939, 152.

4 A. K. Davies, G. A. Gee, J. F. McKellar and G. O. Phillips, *J. Chem. Soc., Perkin Trans. 2*, 1973, 1742.