Photoinduced electron-transfer reactions of homonaphthoquinones with amine and arene donors

Hiroshi Moriwaki, Takumi Oshima and Toshikazu Nagai *
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Machikaneyama 1–16, Toyonaka, Osaka 560, Japan

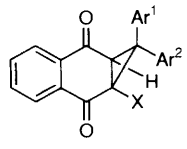
Photoreactions of monoaryl- and diaryl-homonaphthoquinones bearing methyl, chloro and bromo substituents have been studied in the presence of amine and arene donors. The products of these photolyses are dependent on the substituents and the identity of the added donors. Irradiation of bromo-substituted diarylhomoquinones **1a**, **b** with amines such as triethylamine and diethylamine in various aprotic solvents resulted in the formation of (±)- and *meso*-3,3′-bis(diphenylmethylene)-2,2′,3,3′-tetrahydro-2,2′-bi-1,4-naphthoquinones **2a**, **b** *via* the dimerization of intermediary allyl radicals arising from bromide release accompanied by ring-opening of the cyclopropane ring. Besides dimer **2**, a 1:1 amine adduct **4** was also obtained with *N*,*N*-dimethylaniline as donor. However, methyl- and chloro-substituted homoquinones remained intact due to the poor leaving ability of these substituents. A similar reaction of bromo-substituted methylphenylhomoquinones **1e** gave naphthofuran derivative **6** *via* 2-(α-phenylvinyl)-1,4-naphthoquinone **III**. In contrast, photoreactions of **1b** in the presence of arene donors, naphthalene and methoxy-substituted benzenes, gave no dimeric product but instead gave photoisomerized 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone **3** and its photocyclized xanthylium salt **7**. This reaction does not occur in nonpolar solvents. In the case of xanthene as donor, the dimer **2b** was again formed in addition to the **3** and **7**. These reaction features were interpreted in terms of a difference between proton donating ability of the donor cation radicals.

Introduction

Photoinduced electron transfer (PET) reactions have received much attention and intensive studies have been made of a variety of donor–acceptor systems to explore the mechanistic details.[1] During the past decade, PET reactions of cyclopropanes bearing several aryl groups as chromophore have been studied extensively by many workers to gain interesting insights into the physicochemical properties due to the strain of the small ring and to shed light on their potential utility as synthetic intermediates. In most of these cases, the arylcyclopropanes behave as an electron donor due to the high lying HOMO level of the cyclopropane ring and give rise to various types of oxidatively ring-cleaved products. For example, arylcyclopropane radical cations generated from PET reactions undergo nuclophilic attack of alcohols accompanied by cleavage of the cyclopropane ring,[2] *cis–trans* photoisomerization,[3] transformation into propene derivatives,[4] (3 + 2) cycloaddition with vinyl ethers[5] and (4π + 2σ) addition with acceptor 9,10-dicyanoanthracene (DCA).[6] In contrast, only a few examples are known of photoreactions in which arylcyclopropanes act as the acceptor component. These cyclopropanes necessarily contain strong electron withdrawing groups such as CN and halogens. Photoreactions of arylcyclopropanes bearing Br, CO_2R, and CN groups with tertiary amines proceed through cyclopropane radical anions to provide debrominated cyclopropanes,[7] 1:1 amine adducts and reduction products.[8,9]

Recently, we have prepared quinone-fused cyclopropanes, so-called homoquinones, by the 1,3-dipolar addition of diaryldiazomethanes to variously substituted quinones.[10] In view of the electrophilic and conjugative properties of quinones, it is of interest to investigate the PET reaction of these homoquinones in the presence of various types of donor compounds.

This paper deals with the photolysis of monoaryl- and diaryl-substituted homonaphthoquinones **1a–1e** with substituent X (Me, Cl, Br) under the influence of amine and arene donors.[11]



1a X = Br, $Ar^1 = Ar^2$ = *p*-tolyl **1b** X = Br, $Ar^1 = Ar^2$ = Ph
1c X = Cl, $Ar^1 = Ar^2$ = Ph **1d** X = CH_3, $Ar^1 = Ar^2$ = Ph
exo-**1e** X = Br, $Ar^1 = CH_3$, Ar^2 = Ph
endo-**1e** X = Br, Ar^1 = Ph, $Ar^2 = CH_3$

The aim of this study is to explore the different behaviour of the n- and π-donors and to clarify the mechanistic features of photolytic reactions of these homoquinones.

Results and discussion

Photoreaction of diarylhomonaphthoquinones 1a–d in the presence of amine donors

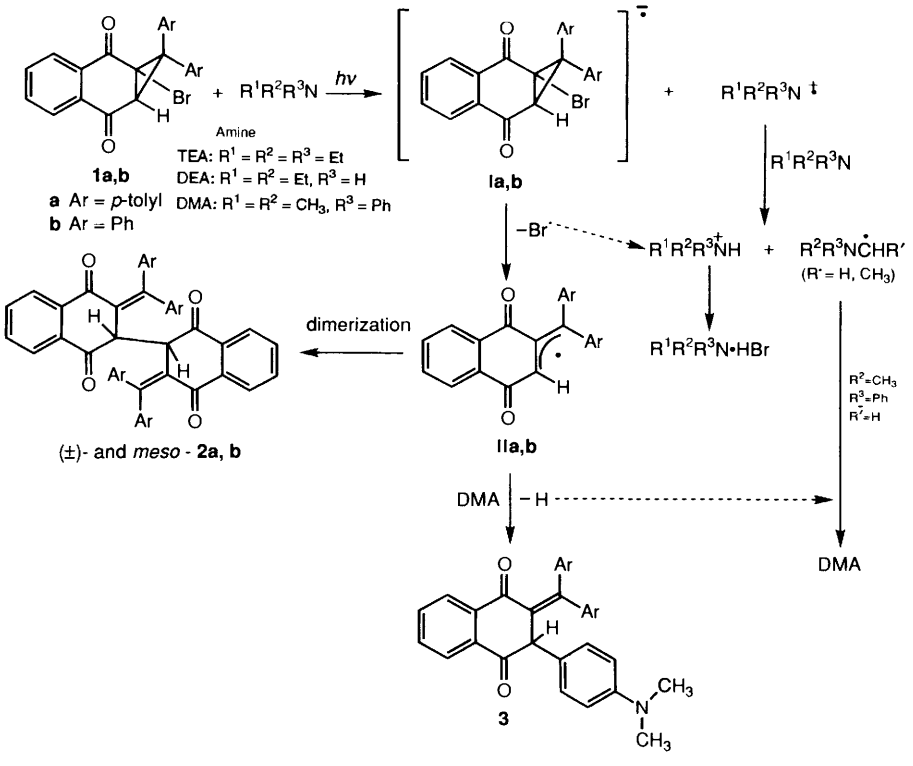
Irradiation of diarylhomonaphthoquinones **1a**, **b** and a 5 equiv. excess of triethylamine (TEA) or diethylamine (DEA) in various solvents under an atmosphere of nitrogen with a high pressure mercury lamp through a filter (> 330 nm) for 2 h gave the dimeric isomers (±)-**2a**, **b** and *meso*-**2a**, **b** in moderate yields together with the hydrogen bromide salts of the respective amines (Table 1 and Scheme 1). In addition to the dimer **2b**, a substantial amount of the 1:1 amine adduct **3** was obtained when **1b** was irradiated in the presence of *N*,*N*-dimethylaniline (DMA).

The structures of **2a**, **b** and **3** were deduced on the basis of the IR, ^1H and ^{13}C NMR and mass spectra. The stereochemistry of the dimers, **2** [(±) and *meso*] was determined by the use of a NMR chiral shift reagent, tris[3-heptafluoropropylhydroxymethylene-(+)-camphorato]europium(III) derivative. The high field methine singlet (δ 4.34 for **2a** and 4.30 for **2b** in $CDCl_3$)

Table 1 Photoreaction of homoquinones **1a–c** and **4a, b** with several amines

Entry	1,4	Donor	Solvent	Irrad. *t*/min	ΔG^a kJ mol^{-1}	Conv. (%)	Yield (%)^b (±)-**2**	*meso*-**2**	(±):*meso*	**4**	Salt
1	**1a**	TEA	MeCN	120		56.7	11.7	10.5	(1.1)	—	55.7
2	**1b**	TEA	MeCN	120	−183	72.6	26.0	23.2	(1.1)	—	78.2
3	**1b**	TEA	MeCN	40		27.3	25.5	21.5	(1.2)	—	86.3
4	**1b**	TEA	EtCN	120		51.1	29.8	22.9	(1.3)	—	68.3
5	**1b**	TEA	CH_2Cl_2	120		69.2	14.7	12.9	(1.1)	—	85.3
6	**1b**	TEA	$MeCO_2Et$	120		69.5	12.5	10.0	(1.3)	—	69.5
7	**1b**	TEA	THF	120		64.8	10.4	7.76	(1.4)	—	63.2
8	**1b**	TEA	C_6H_6	120		62.3	16.7	12.3	(1.3)	—	72.6
9	**1b**	TEA	MeCN–MeOH (90:10)^c	120		37.3	19.8	14.9	(1.3)	—	74.5
10	**1b**	DEA	MeCN	120	−181	57.8	17.4	14.8	(1.4)	—	75.8
11	**1b**	DMA	MeCN	120	−179	63.8	21.2	17.5	(1.2)	15.5	61.4^d
12	**1b**	—	MeCN	120		0	0	0	—	—	0
13	**1b**	TEA	MeCN	0		0	0	0	—	—	0
14	**1c**	TEA	MeCN	120	−212	0	0	0	—	—	0
15	**1d**	TEA	MeCN	120		0	0	0	—	—	0
16	**4a**	TEA	MeCN	120		100	31.6	19.5	(1.9)	—	80.5
17	**4b**	TEA	MeCN	120		100	37.5	23.5	(1.6)	—	85.5

^{a} Calculated according to Weller equation: E_{0-0} of **1b** and **1c** were measured as 3.70 and 3.75 eV, respectively. Reduction potentials of **1b** and **1c** *vs.* SCE are −1.10 and −0.80 V, respectively, in MeCN. The cyclic voltammogram of **1a** revealed an irreversible wave at E_p −1.22 V in MeCN. Oxidation potentials of TEA, DEA and DMA *vs.* SCE are 0.76, 0.78 and 0.81 V, respectively. ^{b} Calculated on consumed **1** or **4**. ^{c} By volume. ^{d} Isolated yield.



Scheme 1

of one isomer was split into two peaks with the same integral strength by the addition of 0.6 equiv. of the shift reagent, whereas the low field methine singlet (δ 4.41 for **2a** and 4.38 for **2b**) of the other isomer was not split. The former high field isomer was assigned as the (±)-form, and the latter as the *meso*-form.

The dimeric isomers (±)- and *meso*-**2b** were photostable on irradiation in the presence of amine. In accord with this, the yield of the dimeric products at high conversion was essentially the same as that at low conversion (entries 2 and 3, Table 1). The values of the (±)/*meso* isomer ratio of **2** were 1.1–1.4 and were not markedly affected by varying the substituent (X) on **1** (entries 1 and 2), solvents (entries 2 and 4–9), as well as donor amines (entries 2, 10 and 11). These reactions did not occur in the absence of amine or in the dark (entries 12 and 13). Furthermore, the replacement of the labile bromo substituent of **1b** by a chloro or methyl group endowed it with photopersistency as noted in **1c, d** (entries 14, 15).

The fluorescences of **1** were quenched by triethylamine. Stern–Volmer plots of the fluorescence quenching in acetonitrile were linear with amine concentration, indicating electron transfer to the singlet excited state of **1**. The value of k_q obtained from the slope of Stern–Volmer plot of **1b** was 2.90×10^9 dm^3 mol^{-1} s^{-1}. Free energy changes (ΔG) calculated according to the Weller equation [12] for the system of **1b** and various amines are all negative. This means electron transfer from amines to excited **1b** should be spontaneous. No new

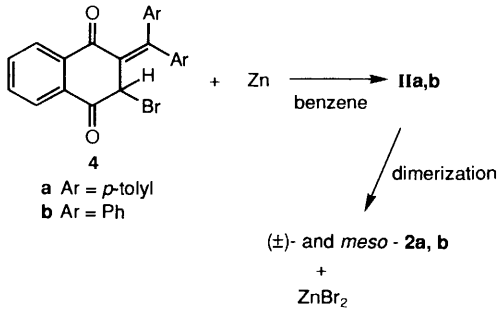
Table 2 Reductive dimerization of **4** by zinc powder in benzene

	Reaction time (h)	Conv. (%)	Yield (%) (±)-**2**	*meso*-**2**	[(±):*meso*]
4a	1	100	32.6	13.1	(2.5)
4b	1	100	49.5	18.9	(2.6)

emission attributable to exciplex fluorescence was observed in the quenching experiments. No essential difference in the absorption spectra was found in mixtures of **1a–d** (6.2 mmol dm^{-3}) and amines at various concentrations (31.0 to 124.0 mmol dm^{-3}). From these facts, it is proposed that the present photoreaction proceeds through the mechanism outlined in Scheme 1.

The first step is photoexcitation of **1** followed by a single electron transfer (SET) from the amine to the excited **1**. The radical anion **Ia, b** thus generated undergoes ring opening with loss of bromide to generate allyl radical **IIa, b**. In contrast, the possible radical anions of **Ic, d** with poor or less labile substituents (Y = Cl, CH_3) will give back the electron to the amine radical cation. The radical **IIa, b** will collapse to give the dimer **2a, b**. The radical cation of the amine will undergo proton abstraction by a second molecule of amine to give the corresponding amino radical and the ammonium ion. At present, it is not clear how the amino radical takes part in the following reaction (see Experimental section). In the case of the DMA donor, formation of the additional product **3** may be due to concomitant nucleophilic attack of the electron-poor radical **IIb** to the *para*-position of a second molecule of DMA, followed by hydrogen abstraction by the initially formed amino radical to regenerate DMA.

Participation of the allyl radicals in the present dimerization process was strongly supported by the observation that the reductive debromination of precursor allyl bromides, **4a, b** with zinc powder also gave (±)- and *meso*-**2a, b** in good yield, most probably *via* the allyl radical **IIa, b** (Table 2, Scheme 2). The



Scheme 2

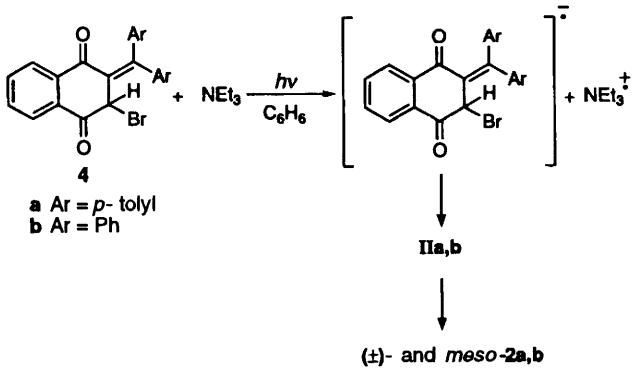
rather higher (±)/*meso* isomer ratios (2.5–2.6) compared with the photoreaction may be ascribed to some surface interaction between the radicals and Zn.[13]

It was also found that the ring-opened **4a, b** on irradiation in the presence of TEA undergoes dimerization to give the dimer **2a, b** and the amine salt of HBr (Scheme 3). This observation offers the possibility of intervention of ring-opened **4a, b** in the course of above photoreaction of **1a, b**. However, the occurrence of **4a, b** in the photoreaction of **1a, b** was explicitly ruled out because a trapping experiment with added MeOH did not provide the expected methanolysis product of **4b** (Table 1, entries 16, 17, *vide infra* for the capture of **4a** by MeOH).

Table 3 Photoreaction of **1e** in the presence of TEA

1e	Solvent	Conv. (%)	Yield (%)[a] **5**	Salt
exo	C_6H_6	69.3	45.9	87.1
exo	MeCN	78.0	39.2	91.1
endo	MeCN	71.2	44.4	90.3

[a] Calculated on consumed **1e**.



Scheme 3

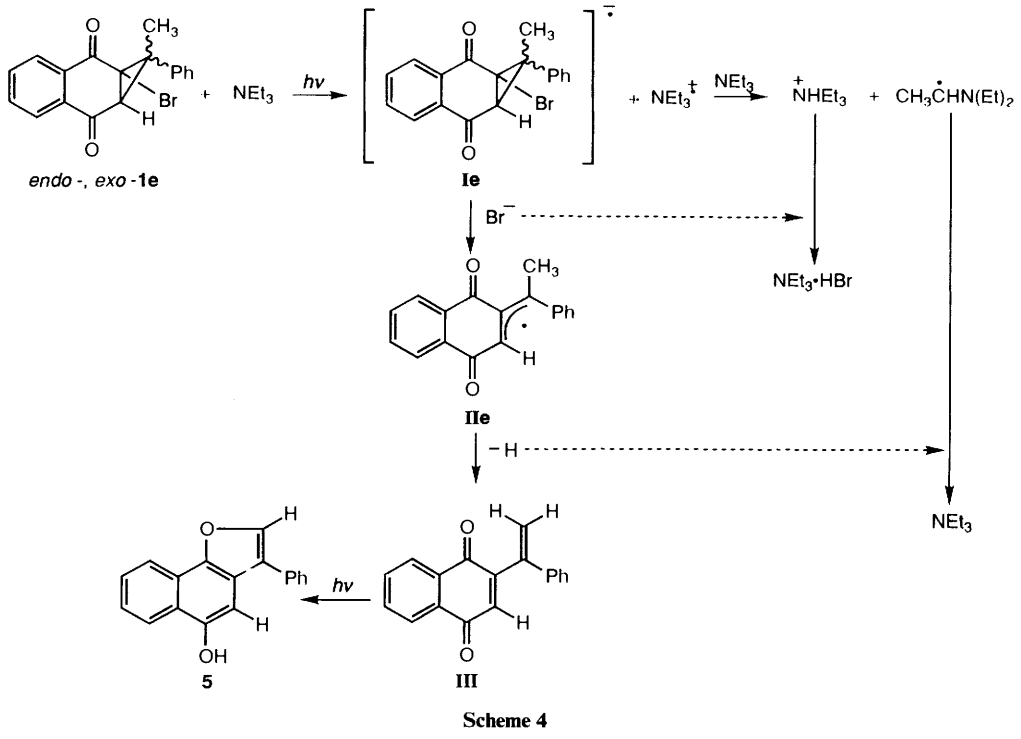
Photoreaction of methylphenylhomonaphthoquinone (*exo*- and *endo*-1e) in the presence of triethylamine (TEA)

A similar irradiation of methylphenylhomonaphthoquinone (*exo*- and *endo*-**1e**) and a 5 equiv. excess of TEA in acetonitrile for 2 h afforded the naphthofuran derivative **5** along with the hydrogen bromide salt of the triethylamine. However, careful ^1H NMR analysis showed neither the formation of plausible dimeric isomers nor the interconversion of *exo*- and *endo*-**1e** under these photolytic conditions (Table 3). These homoquinones remained intact in the absence of amine or when the reaction was performed in the dark. Compound **5** was photostable on irradiation for 2 h in the presence of amine.

Free energy changes (ΔG) calculated for the system of **1e** and triethylamine are all negative (-169 kJ mol^{-1}). Stern–Volmer plots of the fluorescence quenching of **1e** were linear for amine concentration as in the case of **1b**. No new emission spectrum attributable to exciplex fluorescence was observed in the quenching experiments. These facts implied that the photoreaction of **1e** proceeds *via* first a photoinduced electron transfer (PET) as in the case of diarylhomonaphthoquinones. Thus, the mechanism of the photoreaction of **1e** can be visualized as in Scheme 4. The generated radical anion **Ie** undergoes ring opening with loss of bromide to become allyl radical **IIe**. The radical **IIe** leads to 2-(α-phenylvinyl)-1,4-naphthoquinone **III** *via* hydrogen donation to the 1-(*N*,*N*-diethylamino)ethyl radical arising from proton release of the cation radical of TEA. Subsequent photocyclization of **III** gives the naphthofuran derivative **5**. Iwamoto and Takuwa have reported that the direct irradiation of the analogous 2-(α-phenylvinyl)-1,4-benzoquinone resulted in the quantitative formation of the corresponding benzofuran derivative.[14]

Photoreaction of diphenylhomonaphthoquinone 1b in the presence of arene donors

Irradiation of cyclopropane **1b** (6.2 mmol dm^{-3}) and an equimolar amount of naphthalene, dimethoxybenzene or triphenylamine in acetonitrile under an atmosphere of nitrogen for 2 h afforded 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone **4b** and 5-hydroxy-7-phenyl[3,4]benzoxanthylium bromide **7**. It is noted here that the addition of methanol



Scheme 4

Table 4 Photoreaction of diphenylcyclopropanes **1b–d** with arene donors[a]

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

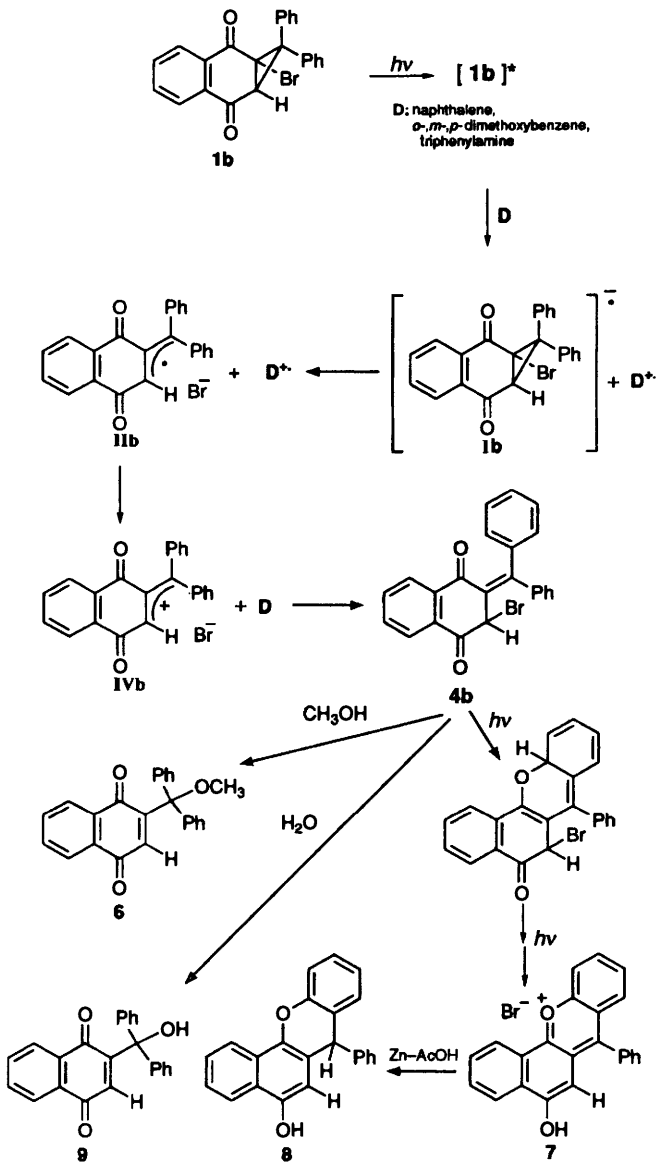
[a] Irradiation time 2 h. [b] Based on consumed **1**. [c] By volume. [d] Isolated yield.

considerably delayed the photoreaction of **1b** and **4** was captured by an SN′ reaction to give 2-[methoxy(diphenyl)-methyl]naphthoquinone **6** (entries 2 and 9). The results and the reaction conditions are shown in Table 4.

The absorption spectrum of **7** recorded in acetonitrile was characterized by several strong absorptions with λ_{max}/nm 240.4 (log ε 4.47), 315.3 (4.26), 395.0 (3.94) and 532.2 (3.70). The IR spectra revealed no carbonyl absorption. The mass spectrum recorded by the electrospray method showed only one peak (*m*/*z* 323, $M^+ - Br$). The reduction of the deep red crystals of **7** with zinc powder in acetic acid gave 5-hydroxy-7-phenyl[3,4]benzoxanthene **8** (74.6% yield). Based on this evidence, we assigned this compound to be the xanthylium salt **7**.

The fluorescence of **1b** was quenched by naphthalene. Stern–Volmer plots of fluorescence quenching are linear *vs.* naphthalene concentration. No new emission ascribable to exciplex fluorescence was observed in the quenching experiments. The value of the free energy change (ΔG) for the system of **1b** and naphthalene was negative (-102.4 kJ mol^{-1}). As in the case of amine donors, no new absorption was observed for the naphthalene donor. Compound **1b** was essentially unreactive in the absence of the donors, in the dark, or in the nonpolar solvent benzene (Table 4, entry 3). The replacement of the bromo substituent of **1b** by a methyl or chloro substituent resulted in the quantitative recovery of **1c**, **d** as noted in the photoreaction of **1c**, **d** (Table 4, entries 7, 8). Based on these facts, a possible mechanism for the photoisomerization of **1b** into the xanthylium salt **7** is given in Scheme 5.

The radical anion **Ib** undergoes ring opening with loss of Br^- to generate allyl radical **IIb**. The next step is a back electron transfer from **IIb** to the radical cation of the arene donor giving the allyl cation **IVb**. For the amine donors, proton abstraction by a second molecule of amine occurred exclusively rather than the back electron transfer, and the radical **IIb** collapsed to the dimer **2b**. Recombination of **IV** with Br^- provides **4b**. The formation of **7** may be rationalized by a photochemical 6π electrocyclization of **4b** and an electron reorganization accompanied by proton migration and Br^- release, as judged from the appreciable decrease in **7** owing to the competitive



Scheme 5

methanolysis of **4b** (entry 2 and 9). In fact, direct irradiation of **4b** in acetonitrile gave **7** in good yield (82.2%).

It is of note that a similar photoreaction of **1b** in the presence of a xanthene donor gave both the dimer **2**, the ring-opened **4** and xanthylium salt **7** together with 9,9′-bixanthenyl. 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.

Conclusions

In the present work, photoreactions of monoaryl- and diarylhomonaphthoquinones **1a–e** with a substituent X (Me, Cl, Br) have been described in the presence of amine donors and arene donors. The photoreactions of diarylhomonaphthoquinone **1a, b** in the presence of triethylamine (TEA) or diethylamine (DEA) gave the dimeric compound **2a, b**, *via* a reductive ring opening followed by dimerization of the resulting allyl radicals. In the case of the *N,N*-dimethylaniline (DMA) donor, an amine adduct **3** was also obtained along with the dimer **2b**. However, methyl- and chloro-substituted **1c, d** remained intact in these photoreactions. A similar photoreaction of methylphenylhomonaphthoquinone **1e** with TEA afforded the naphthofuran derivative **5** *via* the photocyclization of the intermediate 2-(α-phenylvinyl)-1,4-naphthoquinone. The photoreaction of **1b** with arene donors such as naphthalene gave the xanthylium salt **7** *via* photo 6π electrocyclization of the intermediary ring-opened **4b**. Thus, it is concluded that the proton donating ability of the donor plays a decisive role in the product-determining step in such a way that the facile removal of a proton leads to the dimerization of a counter allyl radical by neutralizing bromide, while the poor donation of a proton results in back-electron transfer to afford an allyl cation which is easily trapped by bromide.

Experimental

All melting points were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL EX-270 MHz instrument with Me_4Si (δ 0.00) as internal standard. IR, UV and fluorescence spectra were recorded on a Perkin-Elmer 983G, a Hitachi U-3400 and a Hitachi F-4010 spectrometer, respectively. Mass spectra were taken on a JEOL JMS DX303 mass spectrometer. The light source for all photochemical experiments was an Eikohsha EHB W1-300 300 W high pressure Hg lamp, and the short cut filter used was an Eikohsha glass filter FT-3 (> 330 nm).

Materials

Acetonitrile and propionitrile were refluxed and fractionated over diphosphorus pentaoxide and then over potassium carbonate before use. Benzene and tetrahydrofuran were refluxed over lithium aluminium hydride for 1 day and then fractionated. Dichloromethane and ethyl acetate were distilled over calcium hydride prior to use. All amine and arene donors were of commercial origin and were purified by distillation after drying over NaOH for liquid donors or by recrystallization for solid ones. Diarylhomonaphthoquinones **1a–d** were prepared by the treatment of diphenyl- and bis(*p*-tolyl)-diazomethanes with 2-methyl-, 2-chloro- and 2-bromo-naphthoquinones according to previously reported procedures.[10,15] 2-Bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone **4** was obtained from the thermolysis of **1b** according to the literature method.[10]

Monoarylhomonaphthoquinones *endo*- and *exo*-**1e**† were synthesized by the treatment of 1-phenyldiazoethane with 2-bromonaphthoquinone in benzene for 5 h. The *exo* and *endo* isomers were separated by column chromatography on silica gel using hexane–benzene as eluent. The high melting point isomer was ascertained to be the *endo* isomer on the basis of the NOE between the methyl group at C-7 and the methine proton at C-6.

***exo*-2-Bromo-2,3-dihydro-2,3-[methyl(phenyl)methano]-1,4-naphthoquinone *exo*-1e.** Yield 22.5%, mp 114–115 °C; colourless prisms (from hexane–benzene); ν_{max}(KBr)/cm^{-1} 1677, 1590, 1445, 1353, 1286, 1251, 747 and 695; δ_H 1.48 (s, 3 H) 3.40 (s, 1 H) 7.36–7.43 (m, 5 H) 7.80–7.84 (m, 2 H) and 8.17–8.25 (m, 2 H); *m/z* 340 (M^+) (Found: C, 63.2; H, 3.9. Calc. for $C_{18}H_{13}BrO_2$: C, 63.36; H, 3.8%).

***endo*-2-Bromo-2,3-dihydro-2,3-[methyl(phenyl)methano]-1,4-napthoquinone *endo*-1e.** Yield 4.0%, mp 148–149 °C; colourless needles (from hexane–benzene); ν_{max}(KBr) 1681, 1284, 772 and 709; δ_H($CDCl_3$) 1.92 (s, 3 H), 3.14 (s, 1 H), 6.93–6.98 (m, 5 H), 7.42–7.46 (m, 2 H) and 7.72–7.79 (m, 2 H); *m/z* 340 (M^+) (Found: C, 63.3; H, 3.95. Calc. for $C_{18}H_{13}BrO_2$: C, 63.36; H, 3.84%).

† The stereochemical designations of *exo* and *endo* for compound **1e** relate to the relative orientation of the methyl group (see structure **1e**).

Photoreaction of homonaphthoquinones 1a–d in the presence of triethylamine (TEA) and diethylamine (DEA)

Irradiation of homonaphthoquinones **1a–d** (6.2 mmol dm^{-3}) and an excess of TEA and DEA (5 equiv.) in various solvents was carried out under an atmosphere of nitrogen with a high pressure mercury lamp through a filter (> 330 nm) for 2 h.

The general procedure is represented for the case of **1b** (50.0 mg) and TEA (62.8 mg) in acetonitrile (20 dm^3). After irradiation, the solvent and the excess of amine were evaporated and the reaction mixture was analysed by ^1H NMR spectroscopy to determine the conversion of **1b** and the yield of the dimeric compound **2** using 4-(chloromethyl)biphenyl as internal standard. The reaction mixture was washed with benzene (5 cm^3 × 3) to leave the amine salt of hydrogen bromide (12 mg, 68%). The combined washings were evaporated and the residue was chromatographed on silica gel to give successively unchanged **1b** (11 mg, 22%) and (±)-**2b** (7 mg, 22%) using hexane–benzene as eluent, and *meso*-**2b** (6 mg, 19%) and a second crop of the amine salt (1 mg, 6%) with benzene–diethyl ether as eluent, and finally a considerable amount of intractable resinous material (10 mg) with methanol as eluent. Formation of such resinous unidentified products was also the case for the photoreaction in the presence of DEA and DMA. HPLC analysis of the reaction mixture also showed the presence of at least seven by-products eluted prior to unchanged **1b** and *meso*- and (±)-**2b**. Judging from the proposed mechanism in Scheme 1, some of these products may arise by a side pathway *via* the allyl radical and the amino radical, and also the further photodegradation of these primary adducts. However, we could not isolate them even by careful chromatography on silica gel.

***meso*-3,3′-Bis(diphenylmethylene)-2,2′,3,3′-tetrahydro-2,2′-bi-1,4-naphthoquinone *meso*-2b.** Mp 278–279 °C; pale yellow prisms (from benzene–hexane); ν_{max}(KBr)/cm^{-1} 1686, 1487, 1285, 1242, 1227, 982 and 704; δ_H($CDCl_3$) 4.38 (s, 2 H), 6.73–6.77 (m, 4 H), 7.04–7.08 (m, 4 H), 7.13–7.17 (m, 6 H), 7.21–7.26 (m, 6 H), 7.62–7.66 (m, 4 H) and 7.80–7.86 (m, 4 H); δ_C($CDCl_3$) 59.5, 127.1, 127.2, 127.6, 128.0, 128.2, 128.4, 128.5, 130.3, 133.7, 133.9, 134.8, 136.5, 139.7, 140.2, 154.5, 185.6 and 194.0; *m*/*z* 646 (M^+) (Found: C, 85.4; H, 4.8. Calc. for $C_{46}H_{30}O_4$: C, 85.43; H, 4.68%).

(±)-3,3′-Bis(diphenylmethylene)-2,2′,3,3′-tetrahydro-2,2′-bi-1,4-naphthoquinone (±)-2b. Mp 288–290 °C; pale yellow prisms (from benzene–hexane); ν_{max}(KBr)/cm^{-1} 1694, 1589, 1488, 1281, 1245, 1157, 984 and 703; δ_H($CDCl_3$) 4.30 (s, 2 H), 7.03–7.06 (m, 4 H), 7.14–7.24 (m, 10 H), 7.28–7.34 (m, 6 H), 7.56–7.60 (m, 4 H) and 7.74–7.81 (m, 4 H); *m*/*z* 646 (M^+) (Found: C, 85.5; H, 4.84. Calc. for $C_{46}H_{30}O_4$: C, 85.43; H, 4.68%).

***meso*-3,3′-Bis(di-*p*-tolylmethylene)-2,2′,3,3′-tetrahydro-2,2′-bi-1,4-naphthoquinone meso-2a.** Mp 290–292 °C; yellow prisms (from benzene–hexane); ν_{max}(KBr)/cm^{-1} 1688, 1588, 1289, 1239, 1225, 981 and 728; δ_H($CDCl_3$) 2.25 (s, 6 H), 2.29 (s, 6 H), 4.41 (s, 2 H), 6.61 (d, $J_{AA'}$ 7.91, 4 H), 6.90–7.00 (m, 8 H), 7.02–7.08 (m, 4 H), 7.58–7.68 (m, 4 H), 7.75–7.82 (m, 2 H) and 7.82–7.85 (m, 2 H) (Found: M, 702.28. Calc. for $C_{50}H_{38}O_4$: *M*, 702.28).

(±)-3,3′-Bis(di-*p*-tolylmethylene)-2,2′,3,3′-tetrahydro-2,2′-bi-1,4-naphthoquinone (±)-2a. Mp 287–289 °C; yellow prisms (from hexane–benzene); ν_{max}(KBr)/cm^{-1} 1693, 1589, 1504, 1247, 985, 816 and 728; δ_H($CDCl_3$) 2.25 (s, 6 H), 2.33 (s, 6 H), 4.34 (s, 2 H), 6.91 (d, $J_{AA'}$ 8.25, 4 H), 6.89–7.04 (m, 4 H), 7.07–7.10 (m, 8 H), 7.56–7.88 (m, 4 H) and 7.76–7.79 (m, 4 H); *m*/*z* 702 (M^+) (Found: C, 85.1; H, 5.45. Calc. for $C_{50}H_{38}O_4$: C, 85.44; H, 5.45%).

Photoreaction of homonaphthoquinone 1b in the presence of *N*,*N*-dimethylaniline (DMA)

A similar photoreaction of **1b** and DMA (5 equiv.) in acetonitrile gave the dimeric compound **2b**, 1 : 1 amine adduct **4** and the amine salt. After irradiation, the reaction mixture was analysed by ^1H NMR spectroscopy to determine the conversion of **1b** and the yield of the products as described above. The reaction mixture was washed with benzene (5 cm^3 × 3) to leave the amine salt of hydrogen bromide. The combined washings were evaporated and the residue was chromatographed on silica gel to give successively unchanged **1b** (12 mg, 24%), amine adduct **4** (4 mg, 10.7%), (±)-**2b** (5 mg, 18.4%) eluting with hexane–benzene, and *meso*-**2b** (4 mg, 14.7%) eluting with a mixture of benzene–diethyl ether, and finally an intractable resinous material (7 mg) eluting with methanol.

2-(*p*-Dimethylamino)phenyl-3-diphenylmethylene-2,3-dihydro-1,4-naphthoquinone 4. Mp 122–123 °C; yellow prisms (from hexane–benzene); ν_{max}(KBr)/cm^{-1} 1688, 1515, 1284, 1249, 1232, 1213, 701 and 680; δ_H(CD_3Cl) 2.90 (s, 6 H), 5.06 (s, 1 H), 6.63 (d, $J_{AA'}$ 8.60, 2 H), 7.02–7.13 (m, 4 H), 7.15–7.42 (m, 8 H), 7.63–7.70 (m, 2 H) and 7.93–8.06 (m, 2 H); δ_C($CDCl_3$) 40.31, 61.04, 112.89, 125.00, 126.85, 127.34, 127.93, 128.16, 128.24, 128.31, 128.82, 129.21, 129.36, 133.27, 133.39, 134.03, 134.22, 136.43, 140.14, 141.18, 149.77, 153.31, 190.50 and 195.13 (Found: *M*, 443.1882. Calc. for $C_{31}H_{25}NO_2$: *M*, 443.1887).

Photoreaction of 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone 3b in the presence of triethylamine (TEA)

A similar photoreaction of **3** in the presence of TEA in benzene gave the dimeric compound (±)- and *meso*-**2b** and the amine salt of hydrogen bromide. The yields of **2b** were determined by ^1H NMR spectroscopy as described above.

Reductive dimerization of 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone 3b to give 2b with zinc powder

To a stirred solution of **3b** (100 mg) in benzene (5 cm^3) was added zinc powder (100 mg). After 1 h, the solvent was evaporated and the reaction mixture was analysed by ^1H NMR spectroscopy to determine the yield of dimer **2b** as described above. The solution was evaporated and the residue was chromatographed on silica gel to give (±)-**2b** (31 mg, 38.6%) with benzene as eluent, and *meso*-**2b** (10 mg, 12.5%) with benzene–diethyl ether as eluent.

Photoreaction of homonaphthoquinones *exo*- and *endo*-1e in the presence of triethylamine (TEA) in acetonitrile

The photoreaction of *exo*- and *endo*-**1e** in the presence of TEA in acetonitrile or benzene gave the naphthofuran derivative **6** and the amine salt of hydrogen bromide. The general procedure is represented for the case of *exo*-**1e** (50.0 mg) and TEA (61.2 mg) in acetonitrile (20 cm^3). After 2 h irradiation, the reaction mixture was analysed by ^1H NMR spectroscopy to determine the conversion of *exo*-**1e** and the yield of the naphthofuran derivative **6** as described above. The reaction mixture was washed with benzene (5 cm^3 × 3) to leave the amine salt of hydrogen bromide (11 mg, 62%). The combined washings were evaporated and the residue was chromatographed on silica gel to give successively unchanged *exo*-**1e** (11 mg, 22%), naphthofuran compound **3** (11 mg, 36.2%) eluting with hexane–benzene, and a considerable amount of intractable resinous material (10 mg) eluting with methanol.

5-Hydroxy-3-phenylnaphtho[1,2-*b*]furan 6. Mp 116–117 °C; colourless needles (from hexane–benzene); ν_{max}(KBr)/cm^{-1} 3407, 1595, 1449, 1247, 1067, 764 and 697; δ_H($CDCl_3$) 5.17 (s, 1 H), 7.22 (s, 1 H), 7.36–7.41, (m, 2 H), 7.49–7.57 (m, 3 H), 7.62–7.68 (m, 2 H), 7.88 (s, 1 H) and 8.25–8.31 (m, 2 H); δ_C($CDCl_3$) 100.4, 120.1, 121.3, 122.0, 122.7, 122.9, 123.3, 124.9, 127.1, 127.4, 127.5, 129.0, 132.3, 140.7, 146.7 and 148.0 (Found: M, 260.086. Calc. for $C_{18}H_{12}O_2$: *M*, 260.084).

Photoreaction of homonaphthoquinone 1b in the presence of naphthalene, *o*-, *m*- and *p*-dimethoxybenzenes and triphenylamine in polar solvents

Irradiation of homonaphthoquinone **1b** (6.2 mmol dm^{-3}) and an equivalent amount of naphthalene, dimethoxybenzene and triphenylamine in various solvents under an atmosphere of nitrogen for 2 h with a high pressure mercury lamp (> 330 nm) afforded 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone **3b** and 5-hydroxy-7-phenyl[3,4]benzoxanthylium bromide **7**.

The general procedure is described for **1b** (50.0 mg) and *p*-dimethoxybenzene (17.1 mg) in acetonitrile (20 cm^3). After irradiation, the reaction solution was analysed by UV spectroscopy to determine the yield of the xanthylium salt **7** (60.9% based on consumed **1b**) with the characteristic absorption at λ_{max} 532.2 nm (log ε 3.70). The solvent was evaporated and the reaction mixture was analysed by ^1H NMR spectroscopy to determine the yield of **3** (12.5%) as described above. The reaction mixture was washed with benzene (5 cm^3 × 4) to leave xanthylium salt **7** (6 mg, 54.5% on 22% conversion). The combined extracts were condensed and chromatographed on silica gel to give successively dimethoxybenzene (15 mg), unchanged **1b** (39 mg, 78%) and 2-[hydroxy(diphenyl)methyl]-1,4-naphthoquinone **9** (1 mg, 10.8%) with increasing amounts of benzene in hexane (~ 100% by volume). Compound **9** was derived from hydrolysis of **3**.

5-Hydroxy-7-phenyl[3,4]benzoxanthylium bromide 7. Mp 283 °C; dark red prisms; ν_{max}(KBr)/cm^{-1} 1622, 1601, 1489, 1414, 1377 and 1270; λ_{max}(MeCN)/nm; λ_{max} 240.4 (log ε 4.47), 315.3 (4.26), 395.0 (3.94), and 532.2 (3.70); $\delta_H(CD_2Cl_2)$ 7.71–8.45 (m, 12 H), 8.64–8.68 (d, *J* 9.91, 1 H), 9.13–9.16 (d, *J* 8.58, 1 H) and 11.65 (s, 1 H); *m*/*z* (electrospray method) 323 (M − Br).

2-[Hydroxymethyl(diphenyl)]-1,4-naphthoquinone 9. Mp 154–155 °C; yellow prisms; ν_{max}(KBr)/cm^{-1} 3443, 1663, 1590, 1339, 1301, 1251, 755 and 700; $\delta_H(CDCl_3)$ 5.10 (s, 1 H), 6.30 (s, 1 H), 7.30–7.37 (m, 10 H), 7.73–7.79 (m, 2 H) and 8.02–8.09 (m, 2 H); *m*/*z* 340 (M^+) (Found: C, 81.0; H, 5.0. Calc. for $C_{23}H_{16}O_3$: C, 81.16; H, 4.74%).

Photoisomerization of 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone 3b

Irradiation of a solution of **3b** (100 mg) in acetonitrile (5 cm^3) for 24 h furnished red prisms of **7** (69 mg, 69%) on the glass surface. The filtrate was analysed by UV spectroscopy to determine the yield of the second crop of **7** (13.2%) as described above.

Reduction of xanthylium salt 7 into xanthene with zinc powder in acetic acid

To a stirred solution of **7** (100 mg) in acetic acid (5 cm^3) was added zinc powder (100 mg). After 2 h, the solvent was evaporated and the reaction mixture was chromatographed on silica gel to give **8** (74.6% yield) with hexane–benzene as eluent.

5-Hydroxy-7-phenyl-7*H*-[3,4]benzoxanthene 8. Mp 161–162 °C; colourless needles; ν_{max}(KBr)/cm^{-1} 3520, 1585, 1486, 1451, 1388, 1299, 1260, 1187 and 754; $\delta_H(CD_3Cl)$ 5.00 (s, 1 H), 5.27 (s, 1 H), 6.40 (s, 1 H), 6.94–7.08 (m, 2 H), 7.15–7.30 (m, 7 H), 7.46–7.64 (m, 2 H), 8.05–8.08 (d, *J* 7.92, 1 H) and 8.40–8.43 (d, *J* 7.92, 1 H); $\delta_H(CDCl_3)$ 44.7, 108.7, 116.6, 117.4, 121.6, 121.7, 123.2, 123.7, 124.3, 125.1, 125.8, 126.6, 126.8, 127.8, 128.6, 128.7, 129.8, 139.9, 146.6 and 150.8; *m*/*z* 324 (M^+) (Found: C, 85.2; H, 5.2. Calc. for $C_{23}H_{16}O_2$: C, 85.16; H, 4.97%).

Photoreaction of homonaphthoquinone 1b in the presence of xanthene in acetonitrile

Irradiation of homonaphthoquinone **1b** (50 mg) and an equivalent amount of xanthene in acetonitrile (20 cm^3) for 2 h with a high pressure mercury lamp (> 330 nm) afforded the dimeric compound **2**, the ring-opened **3** and xanthylium salt **7** along with 9,9′-bixanthenyl. After irradiation, the reaction solution was analysed by UV spectroscopy to determine the yield of **7** (38.7%) as described above. The solvent was evaporated and the reaction mixture was analysed by ^1H NMR spectroscopy to determine the yield of **2** [(±) 5.4%; *meso* 3.6% based on the consumed **1b**], **3** (10.9%) and 9,9′-bixanthenyl (15.9%) as described above. The reaction mixture was washed with benzene (5 cm^3 × 4) to leave xanthylium salt **7**. The combined washings were condensed and chromatographed on silica gel to give successively 9,9′-bixanthenyl (2 mg, 13.8%), unchanged **1b** (34 mg, 68%), **9** (1 mg, 7%) and the dimeric compound **2** (1 mg, 9%) with increasing amounts of benzene in hexane (~ 100% by volume).

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