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Photoreaction of homobenzoquinones with amine donors

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The photoreactions of diphenylhomobenzoquinones 1a–d bearing 2-bromo and 2-methyl substituents have been investigated in the presence of amine donors. The products of these reactions are much dependent on the substituents and the nature of added amines. Irradiation of 1-bromo substituted diphenylhomobenzoquinone 1a with triethylamine (TEA) resulted in ring-opening of the fused-cyclopropane moiety to give 2-diphenylmethyl-1,4-benzoquinone 3a. However, the photoreaction of 1a with *N*,*N*-dimethylaniline (DMA) yielded the 1 : 1 aminated bicyclic dione 4a and bis(*p*-dimethylaminophenyl)methane 7 along with 3a. In contrast, irradiation of 1-methyl substituted diphenylhomobenzoquinones 1b–d with TEA brought about hydrogenation of the C=C double bond to give the bicyclic diones 8b–d. Similar photoreaction of 1b,c with DMA provided only the 1 : 1 aminated bicyclic diones 4b,c, although the trimethyl substituted 1d remained essentially intact.

Introduction

Photoinduced electron transfer has been extensively investigated, not only because of its theoretical interest but also because of its importance in the mechanistic elucidation of photoreactions between donor and acceptor molecules.[1-5]

Recently, we reported that irradiation of bromonaphthoquinone-fused diphenylcyclopropane **2**, a so-called homonaphthoquinone, in the presence of alkylamine donors provides the dimer **7** and the hydrogen bromide salts of the amines *via* an initial electron transfer from amine to the excited homoquinone.[6] This photochemical reaction changed dramatically when the amines were replaced by arene donors[7,8] to give a xanthylium salt. This different pattern of behaviour was rationalized in terms of differences in the nature of the donor molecules and their proton donating ability.

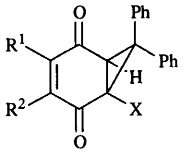
In contrast to the homonaphthoquinones, homobenzoquinones are intriguing because the incorporated π-conjugative enedione unit is expected to undergo a variety of potential photoreactions in analogy with the reaction of enones:[9-11] namely photoinduced hydrogen abstraction, photocycloaddition to olefins and rearrangement.

This paper deals with the photoinduced reaction of 2-bromo- and 2-methyl-substituted diphenylhomobenzoquinones **1** in the presence of triethylamine (TEA) and *N*,*N*-dimethylaniline (DMA). The aim of this study is to explore the scope of the photoreactions of homoquinones and the factors that determine the mechanistic features in comparison with the previous reaction of homonaphthoquinones.[6-8]

Results and discussion

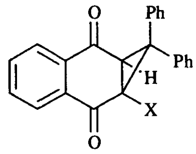
Photoreaction of 2-bromo-substituted diphenylhomobenzoquinone 1a in the presence of amine donors

Irradiation of diphenylhomobenzoquinones **1a** and a 5 equiv. excess of triethylamine (TEA) in benzene under an atmosphere of nitrogen with a high-pressure mercury lamp through a filter (> 330 nm) for 2 h gave the ring-opened hydrogenated product **3a** (49.2%) together with the hydrogen bromide salts of the triethylamine (52.7%) and diethylamine (20.5%) (Scheme 1). Similarly, other alkylamines, diethylamine, tripropylamine, tri-*n*-butylamine, *N*,*N*-diethylaniline (DEA) also provided the quinone **3a** (Table 1). The lack of mass balance in these photoreactions probably arises as a result of the further reaction of **3a** under these photolytic conditions. Indeed, when **3a** was irradiated for 2 h in the presence of 5 equiv. of TEA much of it was used up although the reaction mixture was intractable.



1

a $R^1 = Me, R^2 = H, X = Br$
b $R^1 = Me, R^2 = H, X = Me$
c $R^1 = H, R^2 = Me, X = Me$
d $R^1 = R^2 = Me, X = Me$



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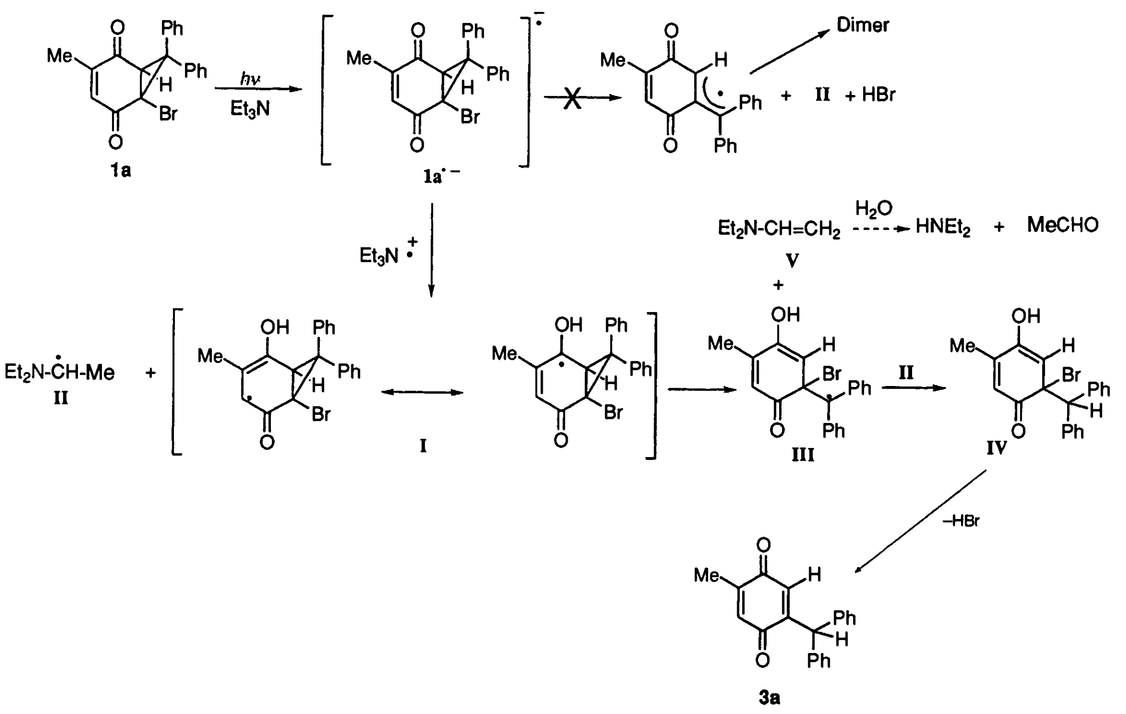
a $X = Br$
b $X = Me$

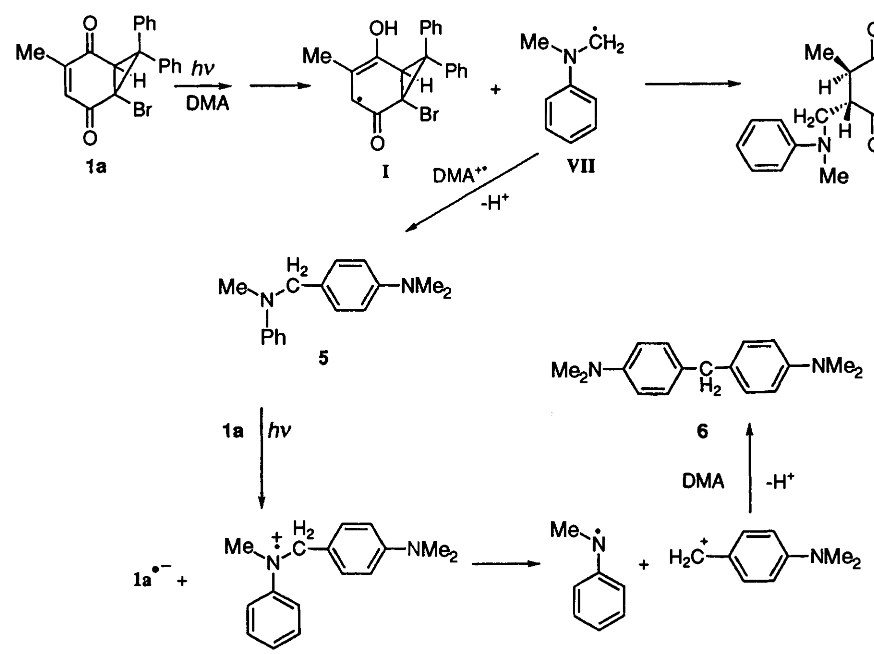
However, when **1a** was irradiated in the presence of *N*,*N*-dimethylaniline (DMA) (for 2 h, conversion; 56.9%), a substantial amount of 1 : 1 aminated adduct **4a** (31.5%) at the C=C double bond and 4,4′-methylenebis(*N*,*N*-dimethylaniline) **6** (16.0%) were obtained, together with **3a** (9.5%) (Scheme 2). The structures of **3a**, **4a** and **6** were deduced on the basis of their IR, ^1H and ^{13}C NMR, and mass spectral results. The stereochemistry of **4a** was determined by NMR analysis (*vide infra*).

These reactions failed to occur in the absence of amine or in the dark. Replacement of amine by a hydrogen donor propan-2-ol also resulted in the quantitative recovery of **1a**. The fluorescence of **1a** (λ_{max} = 420 nm) was quenched by triethylamine in benzene. Stern–Volmer plots of the fluorescence quenching were linear with amine concentration, indicating the electron transfer to the singlet excited state of **1a**. Free-energy changes (ΔG) calculated according to the Weller equation[12] for the system of **1a** and various amines used are all negative (Table 1). This means electron transfer from the amines to the excited **1a** should be spontaneous. No new emission attributable to exciplex fluorescence was observed in the quenching experiments. No essential change in the absorption spectra was found in the mixtures of **1a** (1.0×10^{-3} mol dm^{-3}) and 5 to 20 equiv. of TEA.

From these facts, we propose a possible mechanism for the representative reaction of **1a** with TEA as shown in Scheme 1. The first step is photoexcitation of **1a** followed by a single-electron transfer (SET) from TEA to the excited **1a**. The radical anion $\mathbf{1a}^{\bullet-}$ generated abstracts a proton from $TEA^{\bullet+}$ to be



Scheme 1



Scheme 2

Table 1 Photoreaction of homobenzoquinone **1a** with donors in benzene

Donor	ΔG^a/kJ mol^{-1}	Irrad'n time (t/h)	Conv. (%)^c	Yield (%)^b **3a**
Triethylamine (TEA)	−158	2	75.7	49.2
Triethylamine		Dark	0	0
—		2	0	0
N,*N*-Diethylaniline		2	30	65.7
Triphenylamine	−137	2	0	0
Diethylamine	−156	2	27.9	23.9
Tripropylamine		2	58.5	49.2
Tributylamine		2	54.1	59.8
Naphthalene	−76	2	0	0

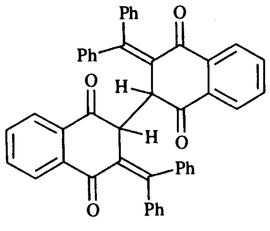
[a] Calculated according to Weller equation: E_{0-0} of **1a** was measured as 3.54 eV. Reduction potential of **1a** *vs.* SCE is −1.15 V in MeCN. [b] Due to the NMR peak areas of methine protons of **3a** and of remaining **1a** with respect to the methylene peak area of 4-(chloromethyl)biphenyl used as an internal standard. [c] Based on **1a** used.

transformed into homobenzosemiquinone **I** and 1-(diethylamino)ethyl radical **II** for TEA donor. The radical **I** undergoes β-fission to become **III**. The radical **III** leads to **3a** by way of H abstraction from the amino radical **II**, tautomerization and the loss of HBr. The resulting enamine **V** easily hydrolyses with residual water to degrade to diethylamine and acetaldehyde.[13]

In the case of the DMA donor, formation of aminated **4a** may be ascribed to the radical coupling of **I** with the counter methylphenylaminomethyl radical **VII** as well as the tautomerization to the keto form (Scheme 2). This amino radical **VII** is also able to participate in the formation of the diamine **6**. Here, the radical **VII** attacks DMA$^{\bullet+}$ at the *para* position to give the dimeric diamine **5** with loss of a proton. The amine **5** will act as a donor component in the photoreaction of **1a**. The diamine radical cation given by the SET reaction dissociates into a methylphenyl aminyl radical and *p*-dimethylaminobenzyl cation. The benzyl cation reacts further with the neutral DMA to afford **6**. Stoichiometrically, two protons can be extruded in the formation of one molecule of **6** as noted in Scheme 2. Such protons seem to be employed preferably in the neutralization of radical anion **1a**$^{\bullet-}$.

It is noteworthy that the DMA donor achieved radical coupling with **I** to give **4a**, but the alkyl amines such as TEA or *N*,*N*-diethylaniline (DEA) did not provide the corresponding amine adduct. This different mode of reaction can be attributed to the bulkiness and hydrogen donating ability of the respective amino radicals. The amino radicals derived from TEA and DEA are secondary and rather crowded around the radical centre which makes coupling with **I** unfavourable. Instead, these radicals are superior hydrogen donating species and facilitate the reducing process leading to **3a**. However, the DMA radical reverses the situation as a result of reduced steric congestion and poor hydrogen donation.

Of special interest is the marked difference in the products between the photoreaction of the homobenzoquinone **1a** used in the present work and that of the homonaphthoquinone **2a** used earlier. As reported earlier, reaction of **2a** in the presence of TEA provided an isomeric mixture of the dimers **7** as a result of coupling of the intermediate allyl radical **VIII**.[6,8] With DMA as a donor, the 1 : 1 amine adduct **9** together with cyclopropane ring-cleavage product **10** and the dimeric product **7** were obtained. These reactions were explained by considering a mechanism involving SET from the amine to the excited **2a**, a ring-opening of the generated radical anion followed by extrusion of bromide to build up the allyl radical as a key intermediate. Participation of such an allyl radical was supported by the observation that thermolysis of the precursor allyl bromide **10** at 100 °C with zinc powder yielded the same dimer as well as the occurrence of reductive dimerization of **VIII**.[6,8]



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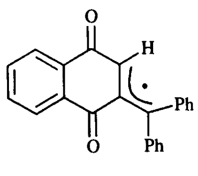
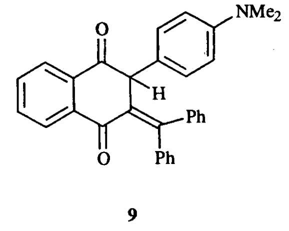


VIII



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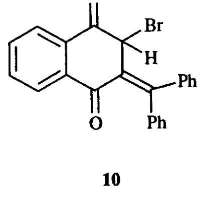

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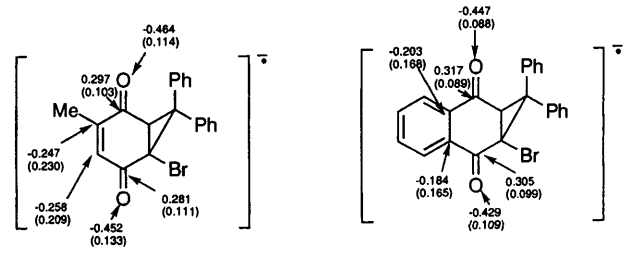

Fig. 1 Calculated charge distributions (upper) and spin density (lower) of the radical anions of **1a** and **2a**

If it were also true that the present homobenzoquinone **1a** follows the similar reaction course as does **2a**, its allyl radical would give rise to the dimer or the same type of amine adduct with DMA. However, possible signals assignable to the expected products were not observed on a careful ^{1}H NMR analysis of the reaction mixture. As shown in Scheme 1, protonation of the radical anion **I** is necessary to produce **3a**, a possible route to the allyl radical being suppressed. Why does the radical anion **1a**$^{\bullet-}$ derived from homobenzoquinone exhibit such a preferred proton acceptability? A comparison of molecular orbital calculations for both radical anions of **1a** and **2** provided no satisfactory account for the preferential proton abstraction of **1a**$^{\bullet-}$ as judged from the almost comparable charge distribution on the quinone framework (Fig. 1).† It is also the same for the spin densities which will relate to the β-fission of the cyclopropane ring to form the allyl radical. Though inconsistent with the calculated distribution of the unpaired electron, we conceive that the fused-benzene nuclei of **2**$^{\bullet-}$ may allow the accumulation of spin density on the adjacent ketyl carbon atom just as in a π-conjugative benzyl radical, by which the β-fission is favoured to give rise to the corresponding allyl radical. As for **1a**$^{\bullet-}$, one can easily imagine that similar stabilization of the radical by allylic conjugation will cause ring-opening of the cyclopropane, but the spin densities of the terminal carbons of the allyl radical are known to be lower than those of the benzyl radical.[14] The reduced liability of **1a**$^{\bullet-}$ toward β-fission may be a cause for the preferable protonation. Unfortunately, however, a clear account for the marked difference in the reaction fashion between **1a**$^{\bullet-}$ and **2a**$^{\bullet-}$ requires further experimentation.

Photoreaction of methyl-substituted diphenylhomobenzoquinone (1b–d) in the presence of amine donors

Irradiation of di- and tri-methyl-substituted diphenylhomobenzoquinones **1b–d** and a 5 equiv. excess of triethylamine (TEA) and diethylamine (DEA) in benzene under an atmosphere of nitrogen with a high-pressure mercury lamp through a short cut filter (> 330 nm) for 5 h gave the hydrogenated products **8b–d** in almost quantitative yields. In contrast, similar photoreaction of dimethyl-substituted **1b,c** in the presence of *N*,*N*-dimethylaniline (DMA) quantitatively provided the aminated products **4b,c**, although trimethyl-substituted **1d** substantially remained intact (Table 2, Scheme 3). The structures of **4b,c** and **8b–d** were illustrated in Scheme 4.

The stereochemistry of **4b,c** and **8b–d** were deduced by the NMR coupling constants between the protons at the 3- and 4-positions, as represented in the case of **8**. The **8b** compound shows two doublet doublet peaks at δ 1.12 (J_1 = 17.16, J_2 = 13.86 Hz) and 2.34 (J_1 = 17.16, J_2 = 6.60 Hz) ppm due to the geminal and vicinal couplings of the methylene at the 3-position. The highfield signal could be assigned to the shielded *syn*-proton and the lowfield signal the *anti*-proton with respect to the fused diphenylcyclopropane ring. The large vicinal

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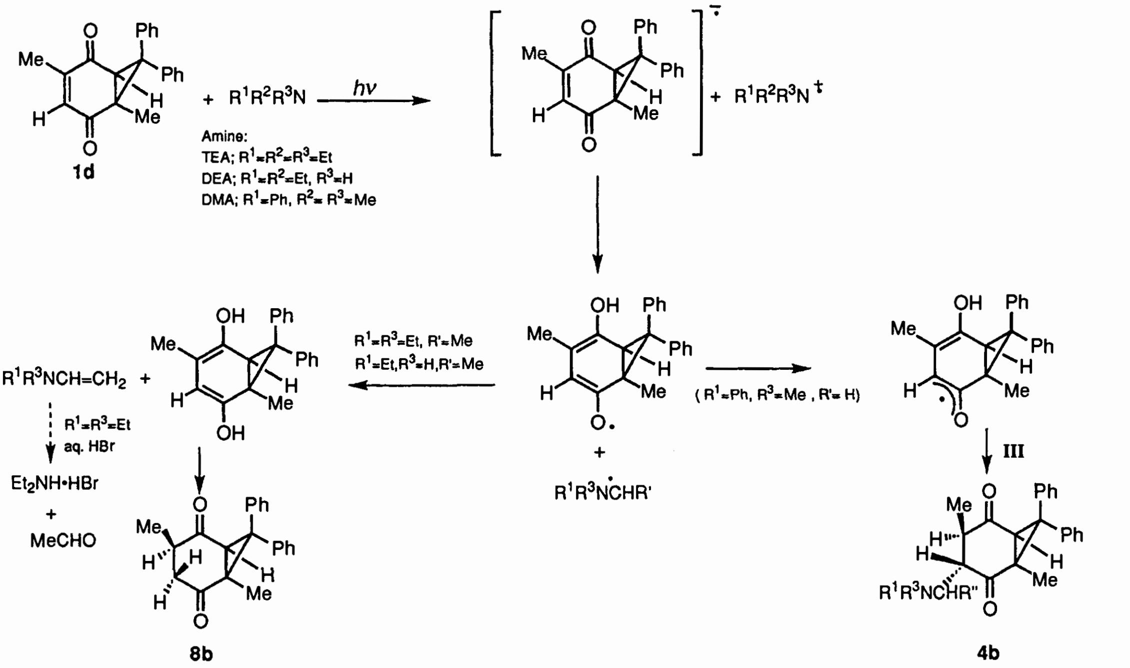
† Molecular orbital calculations by the PM3 method (ref. 15) were performed with the MOPAC94 program using an CAChe system.

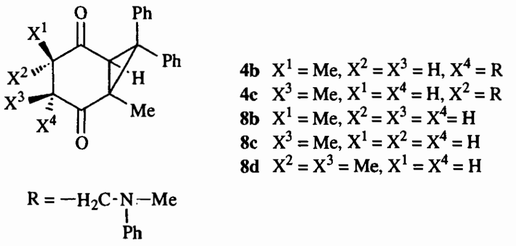
Table 2 Photoreaction of homoquinones **1** and **2** with amines in benzene[a]

Entry	Homoquinone	Donor (Additive)	Conv'n[b] (%)	Yield[c] (%) **4**	Yield[c] (%) **8**
1	**1b**	TEA	100	—	~ 100 (95)
2	**1b**	DEA	10.2	—	~ 100
3	**1b**	DMA	100	~ 100 (83)	0
4	**1b**	Xanthene	7.4	0	0
5	**1b**	Pr^iOH[d]	3.6	0	0
6	**1c**	TEA	100	—	~ 100 (72)
7	**1c**	DMA	100	~ 100 (69)	0
8	**1d**	TEA	100	—	~ 100 (70)
9	**1d**	DMA	4.2	0	0
10	**2b**	TEA	0[e]	0	0
11	**2b**	DMA	0	0	0

[a] Irradiations were carried out on 8.3 mmol dm^{-3} solutions of the homoquinones in benzene (20 cm^3) in the presence of a 5 molar excess of the donors for 5 h with a 300-W high-pressure Hg lamp. [b] Calculated from the NMR peak areas of the methine protons of compounds **1**, **8** and **4** with respect to the methylene peak area of 4-(chloromethyl)biphenyl used as an internal standard. [c] Based on consumed **1** and **2**. Values in parentheses are the isolated yields on silica gel column chromatography. [d] Carried out in Pr^iOH. [e] From refs. 2, 4.



Scheme 3



Scheme 4

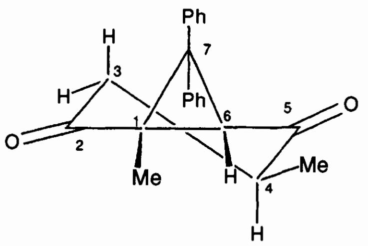


Fig. 2 Half-chair conformation of **8b**

coupling constant (J = 13.86 Hz) of the *syn*-proton suggests an *axial-axial* arrangement with the adjacent methine proton at the 4-position. Indeed, an X-ray crystal structure determination showed the half-chair comformation with a torsion angle of C(2)–C(3)–C(4)–C(5), −36° (Fig. 2).‡ In contrast, the small coupling constant (J 6.60 Hz) of the *anti*-proton can be explained by an *axial-equatorial* arrangement. Similarly, the structure of **8c** was determined. In the case of **8d**, the geminal coupling constant J 6.60 Hz is consistent with the *axial-equatorial* or *equatorial-equatorial* arrangement, but abnormally highfield methyl signals at δ 0.17 and 0.56 must be ascribed to the shielding effects of phenyl ring and the adjacent carbonyl group, indicating its *anti*-periplanar arrangement. The compound **4b,c** revealed *axial-axial* couplings (J 12.53, 12.21 Hz), thereby both the methyl and amino group must occupy the *equatorial* positions. The *anti*-location of the bulky amino group is rationalized by the favoured *anti* attack of the amino radical on the homobenzosemiquinone **IX** (*vide infra*). A careful NMR analysis of the reaction mixture showed stereoselective

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‡ The structure of compound **8b** was confirmed by an X-ray diffraction analysis and will be published separately (*Acta Crystallogr., Sect. C*, in the press).

formation of **4** and **8**, with no evidence of alternative stereoisomers being present.

The fluorescence of **1b** were quenched by TEA and DMA in benzene. Stern–Volmer plots of the fluorescence quenching in benzene were linear with amine concentration, indicating the electron transfer to the singlet excited state of **1b**. No new emission attributable to exciplex fluorescence was observed in the quenching experiments. No essential change in the absorption spectra was found in the mixture of **1b,c,d** (5 mmol dm^{-3}) and a 5–20 equiv. excess of TEA or DMA. Compounds **1b–d** failed to react in the absence of amine or in the dark. Use of xanthene or propan-2-ol in place of amine as a hydrogen source resulted in almost quantitative recovery of **1b** (92.6 and 96.4%) with no detection of the hydrogenated product **8b**. Furthermore, benzo-fusion of the homobenzoquinone framework endowed it with a stability towards photo-hydrogenation and amination as tested for methyl-substituted homonaphthoquinone **2b**.

With these facts in mind, we outline the following mechanism for the photohydrogenation and amination of compounds **1b–d** (Scheme 3).

The first step is photoexcitation of **1** followed by single electron transfer from the amine donor to the excited species. The radical anion **1b**$^{\bullet -}$ so generated abstracts a proton from the radical cation of amine to give homobenzosemiquinone **IX** and the amine radical **II** or **VII**. Here, the hydrogen donating ability of the amine radical plays a decisive role in the subsequent degradation of **IX**. Hydrogen abstraction is an exclusive process for **II** arising from TEA and DEA to provide **8b–d** by way of diketalization. Thus, dealkylation of the amine can be rationalized by hydrolysis of the resulting vinylamine. Absence of such labile hydrogen results in radical coupling to afford the amine adduct **4b,c**, as in the case of DMA.

A preliminary experiment showed that compound **8b** undergo complete deuterium exchange at the 3- and 4-positions, when treated with [$^2H_4$]methanol under the influence of a few drops of TEA or DMA for 5 h in the dark whilst **4b** undergoes exchange only at the 4-position. This finding is consistent with occurrence of keto-enolization of **8** and **4**, and strongly supports the proposed mechanism. Such tautomerization is also the reason for the stereoselective hydrogenation and amination, coupled with the exclusive *anti*-amination. The low conversion (10.2%) of **1b** may be ascribed to the lower oxidation potential and hydrogen donating ability of DEA (0.78 eV *vs.* SCE) compared to TEA (0.76 eV). There was no photoamination of trimethyl-substituted **1d** with DMA probably because of steric hindrance around the relevant C=C double bond. The radical **IX** of **1d** would return the H atom to the amine radical.

Experimental

All melting points were taken on a Yanagimoto micro-melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were obtained on a JEOL EX-270 MHz instrument with SiMe$_4$ (δ 0.00) as an 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 photo 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

Benzene was refluxed over lithium aluminium hydride for 1 day and fractionated. All amine and arene donors were of commercial origin and were purified by distillation after being dried over NaOH for liquid donors or by recrystallization for solid ones. The diarylhomobenzoquinones **1a–d** were prepared from the reaction of diphenyldiazomethanes with 2-bromo-5-methyl-, 2,5-dimethyl-, 2,6-dimethyl- and 2,5,6-trimethylbenzoquinone according to the previous procedures.[8]

Photoreaction of bromo-substituted homonaphthoquinone 1a in the presence of triethylamine (TEA), diethylamine (DEA), tripropylamine, tributylamine and *N*,*N*-diethylaniline

Irradiation of homonaphthoquinones **1a** (2.5 mmol dm^{-3}) and a 5 equiv. excess of amines in benzene 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 **1a** (50.0 mg) and TEA (76.3 mg) in benzene (20 cm^3). After irradiation, the solvent and excess amine were removed by evaporation and the reaction mixture was submitted for ^1H NMR analysis [4-(chloromethyl)biphenyl as internal standard] to determine how much **1a** had been converted and the yield of the hydrogenated compound **3a**. The reaction mixture was washed with benzene (5 cm^3 × 3) to leave the amine salt of hydrogen bromide (7 mg). The combined washings were evaporated and the residue was chromatographed on silica gel with hexane–benzene as eluent to give, successively, unconsumed **1a** (10 mg, 20%) and **3a** (14 mg, 45%) and, finally with methanol as eluent, a large amount of intractable resinous material (7 mg). Similar unidentified resinous products were also formed with other amines. In conformity with this preparative work, HPLC analysis of the reaction mixture showed the presence of at least three by-products eluted prior to the identifiable compounds **1a** and **3a**. On the basis of the proposed mechanism in Scheme 1, some of these products may arise by way of radical side reaction, and also the further photodegradation of these primary adducts. However, careful chromatography on silica gel failed to isolate them.

2-Diphenylmethyl-5-methyl-1,4-benzoquinone 3a. Yellow prisms (from benzene–hexane), mp 150–150.8 °C; ν_{max}(KBr)/cm^{-1} 1646, 1613, 1261, 1262, 1166 and 748; δ_H(CDCl$_3$) 7.36–7.10 (m, 10 H), 6.33 (d, *J* 1.65, 1 H), 6.26 (d, *J* 1.65, 1 H), 5.61 (s, 1 H), 2.04 (d, *J* 1.65, 3 H) (Found: C, 83.4; H, 5.7. Calc. for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%) (Found: *m*/*z*, 288.1154; Calc.: *m*/*z*, 288.11508).

Photoreaction of homobenzoquinone 1a in the presence of *N*,*N*-dimethylaniline (DMA)

A similar photoreaction of **1a** and DMA (5 equiv.) in benzene gave **3a** and the 1 : 1 amine adduct **4a**, bis(*p*-dimethylaminophenyl)methane **7** and amine salt. After irradiation, 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 with hexane–benzene as eluent unconsumed **1a** (24 mg, 43.1%), **3a** (3 mg, 9.5%) and **4a** (10 mg, 31.5%); then with benzene–ether as eluent bis(*p*-dimethylaminophenyl)methane **6** (3 mg, 16%); and, finally, with methanol as eluent intractable resinous material (15 mg). The structure of **6** was confirmed by a comparison of its IR, NMR spectra with those of an authentic specimen.[16]

***rel*-(1*R*,3*S*,4*R*)-1-Bromo-4-methyl-3-methylanilinomethyl-7,7-diphenylbicyclo[4.1.0]heptane-2,5-dione 4a.** Colourless prisms (from benzene–hexane), mp 112–114 °C; ν_{max}(KBr)/cm^{-1} 1669, 1447, 749 and 710; δ_H(CDCl$_3$) 6.9–7.4 (m, 12 H), 6.70 (t, *J* 7.26, 1 H), 6.43 (d, *J* 7.92, 2 H), 3.60 (dd, J_1 14.52, J_2 7.26, 1 H), 3.47 (s, 1 H), 3.40 (dd, J_1 14.52, J_2 3.30, 1 H), 2.86 (s, 3 H), 2.33 (qd, J_1 6.60, J_2 12.87, 1 H), 1.66 (ddd, J_1 7.26, J_2 3.30, J_3 12.87, 1 H), 1.55 (s, 3 H) and 1.02 (d, *J* 6.60, 3 H) (Found: C, 69.05; H, 5.5; N, 2.95. Calc. for $C_{28}H_{26}BrNO_2$: C, 68.86; H, 5.36; N, 2.87%) (Found: *m*/*z*, 487.115. Calc.: *m*/*z*, 487.112).

Photoreaction of methyl-substituted homobenzoquinone 1b–d in the presence of triethylamine (TEA)

The general procedure is represented for the case of dimethyl substituted homobenzoquinone **1b** (50.0 mg) and TEA (83.1

mg) in benzene (20 cm^3). After irradiation, the solvent and volatile matters were removed by distillation *in vacuo* and collected in a chilled trap (−78 °C). The residue was submitted for ^{1}H NMR analysis, with an internal standard, to determine the yield of **8b** as well as the conversion of **1**. Compound **8b** (48 mg, 95%) was isolated by column chromatography on silica gel with benzene as eluent. The distillate was treated with a few drops of hydrobromic acid and dried *in vacuo* to give the hydrogen bromide salt of diethylamine (77%) together with the salt of recovered TEA. Formation of diethylamine apparently indicates that the TEA is dehydrogenated to diethylvinylamine easily capable of being hydrolysed to diethylamine and acetaldehyde.[9] In the case of high-boiling DMA, similar column chromatographic treatment of the reaction mixture containing amine gave, with hexane, recovery of DMA (25 mg) and, with benzene, the aminated compound **4b** (58 mg, 83%).

***rel*-(1*S*,4*R*)-1,4-Dimethyl-7,7-diphenylbicyclo[4.1.0]heptane-2,5-dione 8b.** Colourless prisms (from benzene–hexane), mp 178–179 °C; ν_{max}(KBr)/cm^{-1} 1687, 1447, 1312, 1208, 752 and 712; δ_H(CDCl$_3$) 7.2–7.5 (m, 10 H), 2.88 (s, 1 H), 2.58 (ddq, J_1 13.86, J_2 6.60, J_3 6.60, 1 H), 2.34 (dd, J_1 17.16, J_2 6.60, 1 H), 1.21 (s, 3 H), 1.12 (dd, J_1 17.16, J_2 13.86, 1 H) and 0.81 (d, J 6.60, 3 H); *m/z* (EI) 304 (M$^+$) (Found: C, 82.7; H, 6.7. Calc. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62%).

***rel*-(1*S*,3*S*)-1,3-Dimethyl-7,7-diphenylbicyclo[4.1.0]heptane-2,5-dione 8c.** Colourless prisms (from benzene–hexane), mp 103–104 °C; ν_{max}(KBr)/cm^{-1} 1688, 1446, 1304, 1268, 1042, 709 and 681; δ_H(CDCl$_3$) 7.1–7.4 (m, 10 H), 2.81 (d, J 1.98, 1 H), 2.59 (ddq, J_1 13.53, J_2 6.60, J_3 6.60, 1 H), 2.28 (ddd, J_1 16.50, J_2 6.60, J_3 1.98, 1 H), 1.17 (s, 3 H), 1.04 (dd, J_1 16.50, J_2 13.50, 1 H) and 0.85 (d, J 6.60, 3 H); δ_C(CDCl$_3$) 209.6, 204.8, 140.6, 139.8, 129.6, 129.2, 128.8, 128.5, 127.7, 127.2, 49.1, 44.2, 43.8, 43.7, 43.6, 19.8 and 14.7; *m/z* (EI) 304 (M$^+$) (Found: C, 82.8; H, 6.7. Calc. for $C_{21}H_{20}O_2$: C, 82.86; H, 6.62%).

***rel*-(1*S*,3*S*,4*S*)-1,3,4-Trimethyl-7,7-diphenylbicyclo[4.1.0]-heptane-2,5-dione 8d.** Colourless prisms (from benzene–hexane), mp 161–162 °C; ν_{max}(KBr)/cm^{-1} 1701, 1446, 1233, 751, 711 and 700; δ_H(CDCl$_3$) 7.1–7.5 (m, 10 H), 3.00 (q, d, J_1 7.59, J_2 6.60, 1 H), 2.82 (q, d, J_1 7.58, J_2 6.60, 1 H), 2.76 (s, 1 H), 1.21 (s, 3 H), 0.56 (d, J 7.59, 3 H) and 0.17 (d, J 7.60, 3 H); *m/z* (EI) 318 (M$^+$) (Found: C, 82.8; H, 6.67. Calc. for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96%).

***rel*-(1*S*,3*S*,4*R*)-1,4-Dimethyl-3-methylanilinomethyl-7,7-diphenylbicyclo[4.1.0]heptane-2,5-dione 4b.** Yellow prisms (from benzene–hexane), mp 128–129 °C; ν_{max}(KBr)/cm^{-1} 1685, 1502, 1446, 1190 and 748; δ_H(CDCl$_3$) 6.9–7.4 (m, 12 H), 6.67 (t, J 7.26, 1 H), 6.45 (d, J 8.58, 2 H), 3.65 (dd, J_1 14.85, J_2 7.26, 1 H), 3.19 (dd, J_1 14.85, J_2 3.30, 1 H), 2.87 (s, 1 H), 2.78 (s, 3 H), 2.30 (qd, J_1 12.53, J_2 6.27, 1 H), 1.62 (ddd, J_1 12.53, J_2 7.26, J_3 3.30, 1 H), 1.18 (s, 3 H) and 1.01 (d, J 6.27, 3 H); *m/z* (EI) 423 (M$^+$) (Found: C, 82.0; H, 6.9; N, 3.29. Calc. for $C_{29}H_{29}NO_2$: C, 82.2; H, 6.90; N, 3.31%).

***rel*-(1*S*,3*S*,4*R*)-1,3-Dimethyl-4-methylanilinomethyl-7,7-diphenylbicyclo[4.1.0]heptane-2,5-dione 4c.** Colourless prisms (from benzene–hexane), mp 140–141 °C; ν_{max}(KBr)/cm^{-1} 1685, 1599, 1501, 1208, 748, 709 and 694; δ_H(CDCl$_3$) 6.9–7.4 (m, 12 H), 6.67 (t, J 7.26, 1 H), 6.46 (d, J 7.91, 2 H), 3.60 (dd, J_1 14.52, J_2 7.26, 1 H), 3.26 (dd, J_1 14.52, J_2 3.30, 1 H), 2.94 (s, 1 H), 2.79 (s, 3 H), 2.33 (qd, J_1 6.60, J_2 12.21, 1 H), 1.66 (ddd, J_1 7.26, J_2 3.30, J_3 12.21, 1 H), 1.21 (s, 3 H) and 0.96 (d, J 6.60, 3 H); *m/z* (EI) 423 (M$^+$) (Found: C, 81.3; H, 6.8; N, 3.28. Calc. for $C_{29}H_{29}NO_2$: C, 81.24; H, 6.90; N, 3.31%).

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