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PHOTOINDUCED ELECTRON-TRANSFER REACTIONS OF HOMOQUINONES

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Faculty of Engineering
Osaka University
1996

Preface

The work of this thesis was achieved under the guidance by Professor Emeritus Toshikazu Nagai and Professor Takumi Oshima at the Department of Applied Chemistry, Faculty of Engineering, Osaka University for five years since 1991.

The objective of this thesis is to explore the synthetic utility and mechanistic details of photoinduced electron-transfer reactions of homoquinones.

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March/1996

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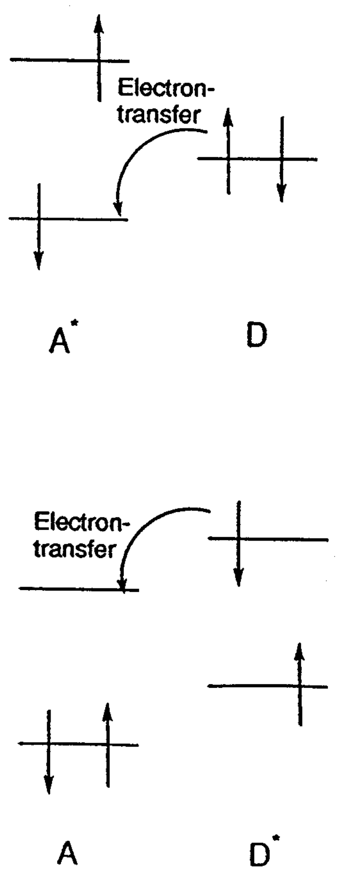
General Introduction

Light-induced reactions between donor(D) and acceptor(A) molecules have recieved much attention from the synthetic and mechanistic view point in recent years[1]. Among these, photoinduced electron-transfer(PET) is the basis of modern method for the formation of the active intermediates *i.e.*, radical ion, under mild conditions[2].

The typical pattern of photoinduced electron-transfer reactions is outlined in Scheme 1. The first step of PET reaction is the transfer of an electron between excited-state and ground-state molecule to generate rasical ions(1). Next is the conversion of radical ions(2) to the products and the back electron transfer to the ground-state reactant(3).



$$A \xrightarrow{h\nu} A^*$$

$$D \xrightarrow{h\nu} D^*$$

$$A^* + D \longrightarrow A^{-\bullet} + D^{+\bullet} \quad (1)$$

$$A + D^* \longrightarrow A^{-\bullet} + D^{+\bullet} \quad (1)$$

$$A^{-\bullet} \longrightarrow \text{Product} \quad (2)$$

$$D^{+\bullet} \longrightarrow \text{Product'} \quad (2)$$

$$A^{-\bullet} + D^{+\bullet} \longrightarrow A + D \quad (3)$$

Scheme 1

Fusion of a functional component to cyclopropane ring is expected to endow a new structural and electronic feature as a candidate for the useful synthetic intermediates, because cyclopropane derivatives undergo a variety of ring-opening reactions[3]. Recently, the preparation of quinone-fused cyclopropanes, so-called homoquinones, in the dipolar addition of diaryldiazomethanes to variously substituted quinones have been reported[4]. In view of the electrophilic and conjugative properties of quinones, it is of interest to obtain insight into the physicochemical properties due to the strained bicyclic systems and to investigate the effect of quinone-fusion on the photolysis of cyclopropane. However, there are only a few studies concerning the skeletal trasformation and the synthetic uses of these ring-condensed systems[5].

The thesis deals with the photoinduced electron-transfer reactions of diaryl-substituted homobenzoquinones and homonaphthoquinones. The aim of this study is to explore the basic structual and mechanistic features of photoreaction of these homoquinones.

The present thesis is consist of three chapters as follows.

The chapter 1 deals with the photoinduced electron-transfer reactions of diaryl-substituted homonaphthoquinones in the presence of alkyl amine or aromatic donors and discusses the effect of the proton donating ability of donor.

The chapter 2 deals with the photoinduced electron-transfer reactions of 2-methyl and 2-bromo-substituted 5-methyl-homobenzoquinones in the presence of amine donors. The factors that determine the mechanistic features are discussed in comparison with the homonaphthoquinone. Furthermore, the X-ray diffraction analysis of trans- 1,4-dimethyl-7,7-dipheny-bicyclo[4.1.0.]hepta-2,5-dione is also described.

The chapter 3 deals with the intramolecular photoinduced electron-transfer reactions of donor-substituted homonaphthoquinones. The mechanism of the photoreaction is discussed in terms of the Coulomnb assistance of added $Mg(ClO_4)_2$.

This thesis are comprised of the following papers.

(1) Photoinduced Reductive Cleavage of Diarylcyclopropanes fused with Bromonaphthoquinone in the Presence of Amines.
Hiroshi Moriwaki, Takumi Oshima and Toshikazu Nagai
J. Chem. Soc., Chem. Commun., 1994, 255-256.

(2) Photoisomerization of Bromonaphthoquinone-fused Diphenylcyclopropane into Xanthylium Salt in the Presence of Arene Donors.
Hiroshi Moriwaki, Takumi Oshima and Toshikazu Nagai
J. Chem. Soc., Chem. Commun., 1994, 1681-1682.

(3) Photoinduced Electron-Transfer Reactions of Homonaphthoquinones with Amine and Arene Donors.
Hiroshi Moriwaki, Takumi Oshima and Toshikazu Nagai

J. Chem. Soc., Perkin Transactions 1, 1995, 2517-2523.

(4) Photoreactions of Homoquinones with Amine Donors.
Hiroshi Moriwaki, Takashi Matsumoto, Toshikazu Nagai and Takumi Oshima
J. Chem. Soc., Perkin Transactions 1, in press.

(5) Conversion of Donor-substituted Homonaphthoquinones into indenonaphthoquinones via intramolecular Photoinduced Electron-transfer.
Hiroshi Moriwaki, Kazuaki Fukushima, Toshikazu Nagai and Takumi Oshima
J. Chem. Soc., Chem. Commun., in press.

(6) Half-chair Conformation of trans- 1,4-dimethyl-7,7-diphenybicyclo[4.1.0.]hepta-2,5-dione, $C_{21}H_{20}O_2$.
Hiroshi Moriwaki, Tatsuya Kawamoto and Takumi Oshima
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Chapter 1.

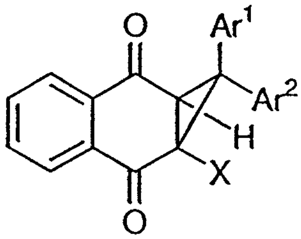
Photoinduced Electron-Transfer Reactions of Homonaphthoquinones

1-1 Introduction

During the past decade, photoinduced electron-transfer (PET) reactions of cyclopropanes bearing several aryl groups as chromophore have been studied extensively by many workers to get interesting insights on the physicochemical properties due to the strain of the small ring and to shed light on potential utility of them as synthetic intermediates. In most of these cases, arylcyclopropanes behave as the electron donor due to the high lying HOMO level of cyclopropane ring and give rise to various type of oxidatively ring-cleaved products. For example, arylcyclopropane radical cations generated from PET reaction undergo nucleophilic attack of alcohols accompanied by cleavage of cyclopropane ring[1], *cis-trans* photoisomerization[2], transformation into propene derivative[3], (3+2) cycloaddition with vinylethers[4], and ($4\pi+2\sigma$) addition with acceptor 9,10-dicyanoanthracene (DCA)[5]. In contrast, only a few examples are known about photoreactions in which arylcyclopropanes play 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[6], 1:1 amine adducts and reduction product[7,8].

This chapter 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.

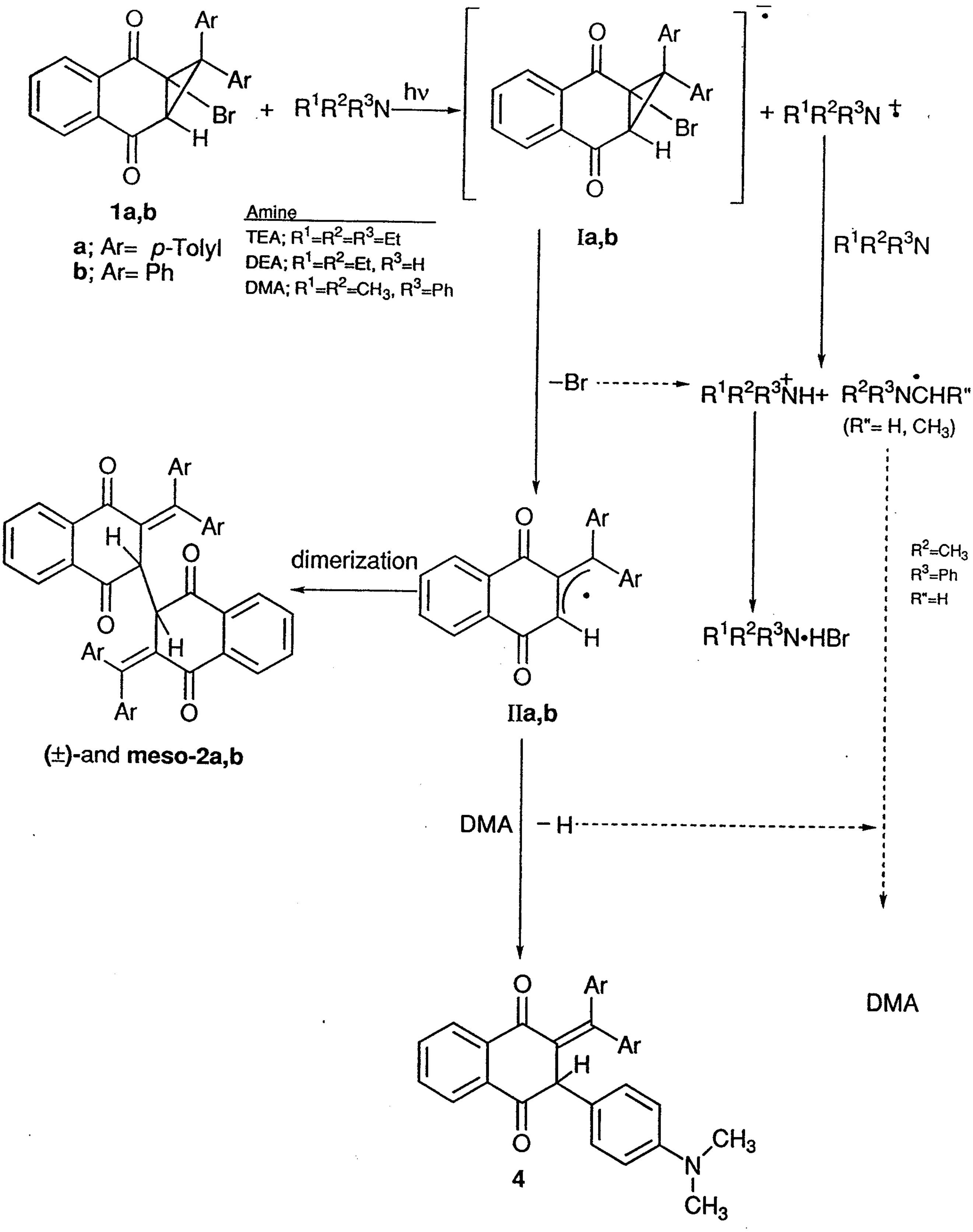
The aim of this study is to explore the distinct behavior between the n- and π-donors and to clarify the mechanistic features of photolytic reactions of these homoquinones.



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

1-2 Reactions with alkyl amine donor

Irradiation of diarylhomonaphthoquinones (**1a,b**) and 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 (>330nm) for 2h 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 1:1 amine adduct **4** was obtained when **1b** was irradiated in the presence of *N,N'*-dimethylaniline (DMA).



1a,b
a; Ar= p-Tolyl
b; Ar= Ph
hv
Amine
TEA; R1=R2=R3=Et
DEA; R1=R2=Et, R3=H
DMA; R1=R2=CH3, R3=Ph
Ia,b
R1R2R3N
−Br
R1R2R3NH+ R2R3NCHR"
(R"= H, CH3)
R2=CH3
R3=Ph
R"=H
dimerization
(±)-and meso-2a,b
IIa,b
R1R2R3N•HBr
DMA
− H
DMA
4

Scheme 1

Table 1 Photoreactions of homonaphthoquinones **1a-c** and **3a,b** with several amines

Entry	1,3	Donor	Solvent	Irrad. time / min	ΔG^a kJ / mol	Yield(%)[b] (±)-2	*meso* -2	(±)/*meso*	4	salt
1	**1a**	TEA	CH_3CN	120		11.7	10.5	1.1	—	55.7
2	**1b**	TEA	CH_3CN	120	-183	25.9	23.2	1.1	—	78.2
3	**1b**	TEA	CH_3CN	40		25.5	21.5	1.2	—	86.3
4	**1b**	TEA	C_2H_5CN	120		29.8	22.9	1.3	—	68.3
5	**1b**	TEA	CH_2Cl_2	120		14.7	12.9	1.1	—	85.3
6	**1b**	TEA	CH_3CO_2Et	120		12.5	10.1	1.3	—	69.5
7	**1b**	TEA	THF	120		10.4	7.76	1.4	—	63.2
8	**1b**	TEA	C_6H_6	120		16.7	12.3	1.3	—	72.6
9	**1b**	TEA	c	120		19.8	14.9	1.3	—	74.5
10	**1b**	DEA	CH_3CN	120	-181	17.4	14.8	1.4	—	75.8
11	**1b**	DMA	CH_3CN	120	-179	21.2	17.5	1.2	15.5	61.4[d]
12	**1b**	—	CH_3CN	120		0	0	—	—	0
13	**1b**	TEA	CH_3CN	0		0	0	—	—	0
14	**1c**	TEA	CH_3CN	120	-212	0	0	—	—	0
15	**1d**	TEA	CH_3CN	120		0	0	—	—	0
16	**3a**	TEA	CH_3CN	120		31.6	19.5	1.9	—	80.5
17	**3b**	TEA	CH_3CN	120		37.5	23.5	1.6	—	85.5

[a] Calculated according to Weller equation; $E_{0\text{-}0}$ of **1b** and **1c** was measured to be 3.70and 3.75 eV. Reduction potential of **1b** and **1c** vs. SCE is -1.10 and -0.80 V in MeCN. The cyclic voltammogram of 1a revealed an irreversible wave at Ep=-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 the Consumed **1** or **3**. [c] MeOH/MeCN= 10/90 by volume. [d] Isolated yield.

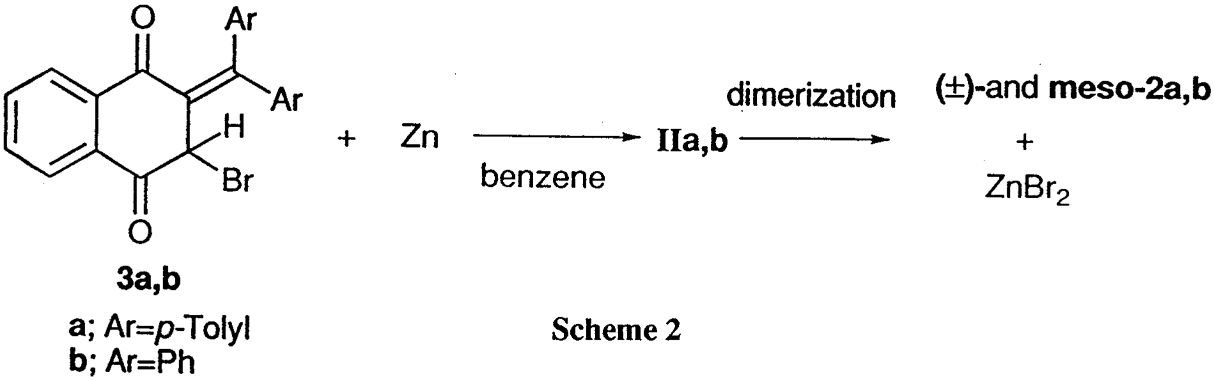
The structures of **2a,b** and **4** were deduced on the basis of the IR, ^1H and ^{13}C NMR, and mass spectra. Stereochemistry of dimers, **2**[(±) and *meso*], was determined by using a NMR chiral shift reagent, tris[3-heptafluoropropylhydroxy-methylene-(+)-camphorato]europium(III) derivative. The high field methine singlet (4.34 ppm for **2a** and 4.30 for **2b** in $CDCl_3$) of one isomer was split into two peaks with the same integral strength by adding 0.6 equiv. of the shift reagent, whereas the low field methine singlet (4.41 ppm for **2a** and 4.38 for **2b**) of another isomer was not split. The former high field isomer was assigned as (±)- form, and the latter one as *meso*-form.

The dimeric isomers (±)-and *meso*-**2b** were photostable on irradiation in the presence of amine. In harmony with this fact, the yield of the dimeric products at high conversion was essentially the same as that at low conversion(entry 2 and 3, Table 1). The values of (±)/*meso* isomer ratio of **2** were in the range of 1.1-1.4 and were not markedly affected by varying the substituent (X) of **1** (entry 1 and 2), solvents (entry 2, and 4-9), as well as donor amines (entry 2, 10, and 11). These reactions did not occur in the absence of amine or in the dark (entry 12 and 13). Furthermore, the replacement of the labile bromo substituent of **1b** by chloro or methyl group endowed it with photopersistency as noted in **1c,d** (entry 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 the electron transfer to the singlet excited state of **1**. Value of k_q obtained from the slope of Stern-Volmer plots of **1b** was 2.90 $\times 10^9$ M^{-1} s^{-1}. Free energy changes (ΔG) calculated according to the Weller equation [9] 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 emission attributable to exciplex fluorescence was observed in the quenching experiments. No essential change in the absorption spectra was found in the mixture of **1a-d** and amines with various concentrations (5 to 20 equiv. excess). 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, possible radical anion of **Ic,d** with poor or less labile substituents (Y=Cl,CH_3) will give back the electron to the amine radical cation. The alive radical **IIa,b** will collapse to dimer **2a,b**. The radical cation of amine will suffer proton abstraction by a second molecule of amine to give the corresponding amino radical and the ammounium ion. At present, it is not clear how the amino radical would take part in the following reaction; see Experimental Section. In the case of DMA donor, formation of the additional product **4** may be due to the concomitant nucleophilic attack of electron-poor radical **IIb** to the para-position of a second molecule of DMA, followed by hydrogen abstraction by 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, **3a,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). Rather higher (±)/*meso* isomer ratios (2.5-2.6) compared to the photoreaction may be ascribed to some surface interaction between the radicals and Zn[10].

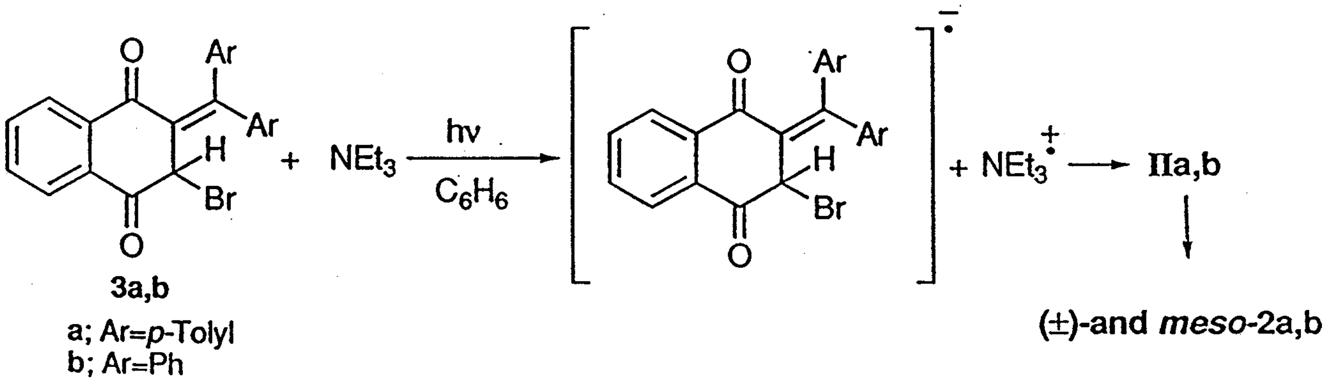


Scheme 2

Table 2 Reductive dimerization of **5** with zinc powder in benzene

	reaction time/h	Conv.(%)	Yield(%) (±)-2	Yield(%) *meso* -2	(±) : meso
3 a	1	100	32.6	13.1	2.5
3 b	1	100	49.5	18.9	2.6

It was also found that the ring-opened **3a,b** on irradiation in the presence of TEA undergoes the dimerization to give dimer **2a,b** and amine salt of HBr (Scheme 3). This observation offers a possibility of intervention of ring-opened **3a,b** in the course of above photoreaction of **1a,b**. However, the occurrence of **3a,b** in the photoreaction of **1a,b** was explicitly ruled out because a trapping experiment under the influence of added CH3OH did not provide the expected methanolysis product of **3b** (Table 1, entry 16,17, vide infra for the capture of **3a** by CH3OH).



Scheme 3

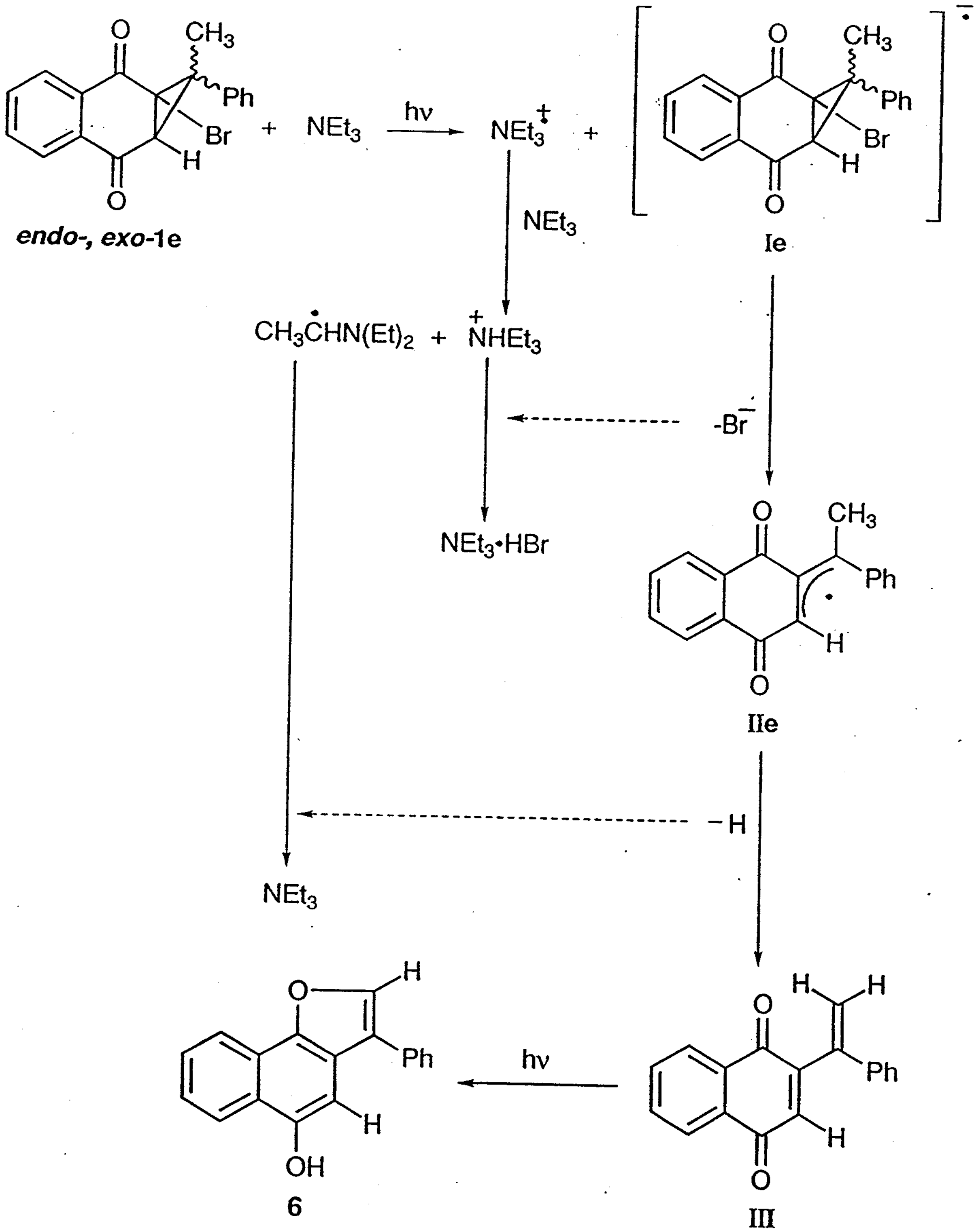
Similar irradiation of methylphenylhomonaphthoquinone (*exo*- and *endo*-**1e**) and 5 equiv. excess of TEA in acetonitrile for 2h afforded the naphthofuran derivative **6** (37.2, 44.4%) along with the hydrogen bromide salts of the triethylamine. However, careful ^1H NMR analysis showed neither the 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 in the dark reaction. The compound **6** were photostable on 2h irradiation in the presence of amine.

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

1e	Solvent	Conv.	Yield(%)[a] 5	salt
exo	C_6H_6	69.3	45.9	87.1
exo	CH_3CN	78.1	39.2	91.1
endo	CH_3CN	71.2	44.4	90.3

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

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 implised that the photoreaction of **1e** proceeds via first photoinduced electron transfer (PET) as in the case of diarylhomonaphthoquinones. Thus, the mechanism of photoreaction of **1e** can be visualized in Scheme 4.


endo-, exo-1e
hν
NEt3
Ie
CH3ĊHN(Et)2 + NHEt3
-Br
NEt3•HBr
IIe
−H
NEt3
hν
6
III

Scheme 4

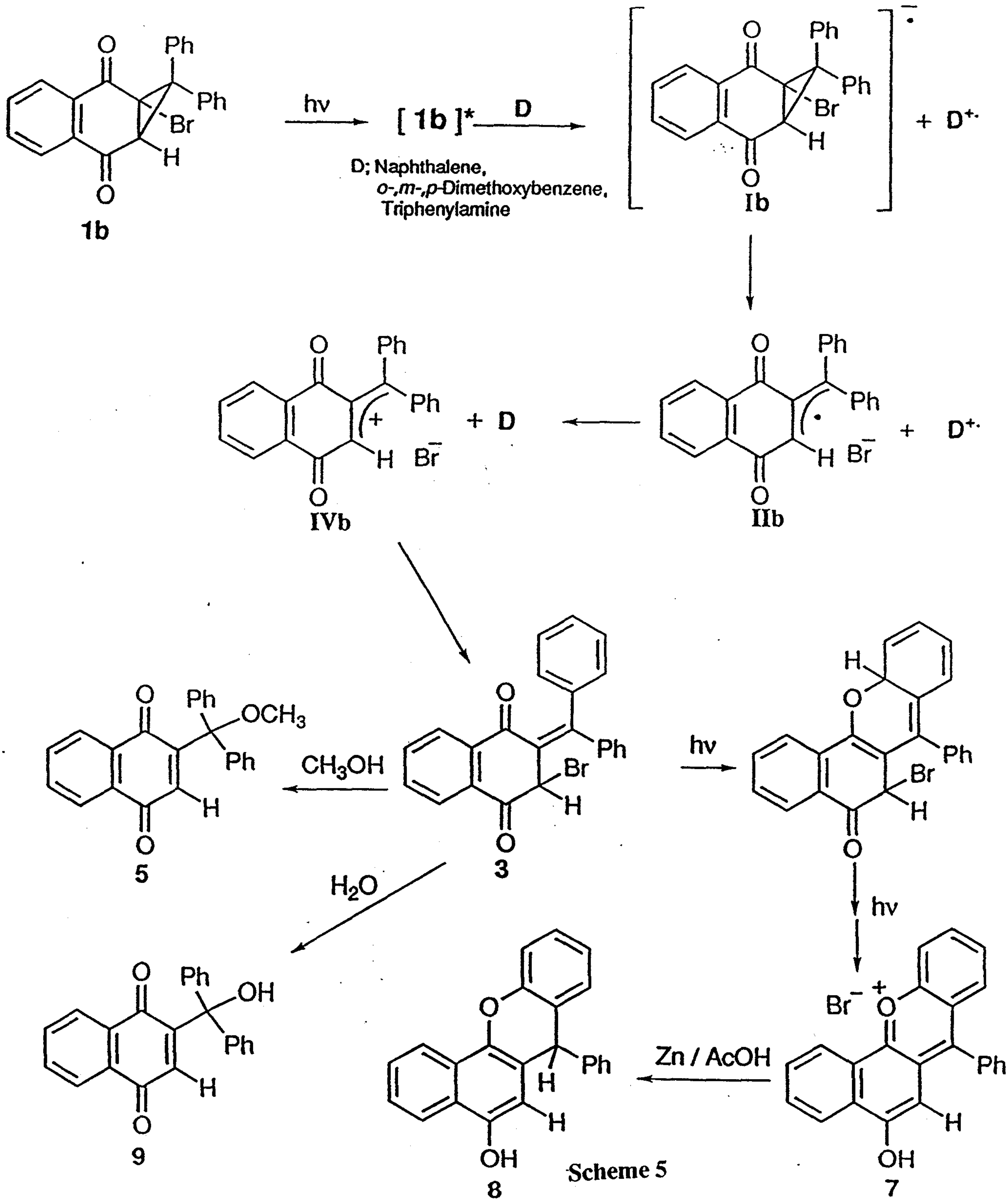
The generated radical anion **Ie** undergoes ring opening with loss of bromide to become allyl radical **IIe**. The radical **IIe** will lead to 2-α-phenylvinyl-1,4-naphthoquinone (**III**) via hydrogen donation to the 1-(*N,N*-diethylamino)ethyl radical arising from proton release of cation radical of TEA. Subsequent photocyclization of **III** gives the naphthofuran derivative **6**. Indeed, Iwamoto et al. reported the direct irradiation of analogous 2-α-phenylvinyl-1,4-benzoquinone resulted in the quantitative formation of the corresponding benzofuran derivative[11].

1-3 Reactions with aromatic donor

Irradiation of cyclopropane **1b** (6.2 mM) and an equimolar amount of naphthalene, dimethoxybenzene or triphenylamine in acetonitrile under an atmosphere of nitrogen for 2h afforded 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone **3** and 3,4-benzo-2-hydroxy-9-phenylxanthylium bromide **7**. It is noted here that additive methanol considerably delayed the photoreaction of **1b** and captured **3** by $S_N{}'$ reaction to give 2-(α-methoxy)diphenylmethylnaphthoquinone **5** (entry 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}=240.4 nm (logε=4.47), 315.3 (4.26), 395.0 (3.94) and 532.2 (3.70). The IR spectra revealed no carbonyl absorption. Mass spectrum by electrospray method showed only one peak (*m/z* 323, M^+-Br). The reduction of the deep red crystal with zinc powder in acetic acid gave 3,4-benzo-2-hydroxy-9-phenylxanthene **5** (74.6% yield). Based on these 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 for naphthalene concentration. No new emission ascribable to exciplex fluorescence was observed in the quenching experiments. The value of free energy change (ΔG) for the system of **1b** and naphthalene was negative (-102.4 kJ/mol). As in the case of amine donors, no new absorption was observed for naphthalene donor. The compound **1b** was essentially unreactive in the absence of the donors, in dark, or in nonpolar solvent benzene (Table 4, entry 3). The replacement of the bromo substituent of **1b** by methyl group or chloro substituent resulted in the quantitative recovery of **1c,d** as noted in the photoreaction of **1c,d** (Table 4, entry 7,8). From these facts, possible mechanism of the photoisomerization of **1b** into the xanthylium salt **7** can be seen in Scheme 5.



Scheme 5

Table 4 Photoreaction of homonaphthoquinones(**1b-d**) with

Entry	Cyclo-propane	Donor	Solvent	Conv.(%)	Yield[b](%) 3	7	5
1	**1b**	naphthalene	CH_3CN	13.7	9.5	60.6	—
2	**1b**	naphthalene	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	CH_3CN	22.1[d]	12.5	60.9	—
6	**1b**	m-dimethoxybenzene	CH_3CN	12.1[d]	10.3	46.1	—
7	**1b**	o-dimethoxybenzene	CH_3CN	13.8	10.8	63.1	—
8	**1b**	triphenylamine	CH_3CN	48.5	4.8	69.5	—
9	**1b**	triphenylamine	c	19.5	0	35.3	64.1
10	**1c**	naphthalene	CH_3CN	0	0	0	—
11	**1d**	naphthalene	CH_3CN	0	0	0	—

a Irradiation time: 2h. b Based on consumed **1**. c MeOH/MeCN= 10/90 by volume. d Isolated yield.

The radical anion **Ib** undergoes ring opening with loss of Br^- to generate allyl radical **IIb**. Next step is the back electron transfer from **IIb** to the radical cation of arene donor giving the allyl cation **IV**. In the case of amine donor, proton abstraction by a second molecule of amine exclusively occurred rather than the back electron transfer, and the radical **IIb** collapsed to the dimer **2b**. Recombination of **IV** with Br^- will provide **3b**. Formation of **7** may be rationalized by the photochemical 6π electrocyclization of **3b** and the electron reorganization accompaied by proton migration and Br^- release, as judged from the appreciable decrease of **7** owing to the competitive methanolysis of **3b** (entry 2 and 9). In fact, direct irradiation of **3b** in acetonitrile gave **7** in good yield (82.2%).

It is of much interest that similar photoreaction of **1b** in the presence of xanthene donor gave both the dimer **2**, the ring-opened **3** 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.

1-4 Conclusion

In the present chapter, 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 the reductive ring opening followed by dimerization of the resulting allyl radicals. In the case of *N,N*-dimethylaniline (DMA) donor, an amine adduct **4** was also obtained along with the dimer **2b**. However, methyl- and chloro-substituted **1c,d** remained intact in these photoreactions. Similar photoreaction of methylphenylhomonaphthoquinone (**1e**) with TEA afforded the naphthofuran derivative (**6**) via the photocyclization of the intermediate 2-α-phenylvinyl-1,4-naphthoquinone. The photoreaction of **1b** with the arene donors such as naphthalene gave xanthylium salt **7** via photo 6π electrocyclization of intermediary ring-opened **3b**. Thus, it is concluded that the proton donating ability of donor plays a decisive role in the product-determining step in such a way that the facile removal of proton leads to the dimerization of counter allyl radical by nutralizing bromide, while the degenerated donation of proton results in back-electron transfer to afford allyl cation easily trapped by bromide.

1-5 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 Me_4Si (δ 0.00) as an internal standard. IR, ultraviolet and fluorescense 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 300W high pressure Hg lamp, and the short cut filter used were an Eikohsha glass filter FT-3 (>330nm).

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 fractionated. Dichloromethane and ethyl acetate were distilled over calcium hydride prior to use. All amine and arene donors were 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 from the reaction of diphenyl and bis(*p*-tolyl)diazomethanes with 2-methyl-, 2-chloro-, and 2-bromonaphthoquinones according to the previous procedures[12,13]. 2-Bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone (3) was obtained from the thermolysis of **1b** according to the method of literature[12].

Monoarylhomonaphthoquinones (*endo*- and *exo*-**1e**) were synthesized from the reaction of 1-phenyldiazoethane with 2-bromonaphthoquinone in benzene for 5h. *Exo* and *endo* isomer were separated by column chromatography on silica gel by using hexane-benzene as an eluent. The high melting point isomer was ascertained as *endo* isomer on the basis of the n.O.e. between the methyl group at C-7 and the methine proton at C-6 position.

Exo-1- bromo-3,4-benzo-7-methyl-7-phenylbicyclo-2,5-dione (exo-1e).

Yield 22.5%; m.p. 114-115 °C ; colorless prisms (from hexane-benzene) ; IR(KBr) 1677, 1590, 1445, 1353, 1286, 1251, 747, 695 cm^{-1}.

NMR($CDCl_3$) δ 1.48 (s,3H) 3.40 (s,1H) 7.43-7.36 (m,5H) 7.80-7.84 (m,2H) 8.17-8.25 (m,2H) MS *m/e* 340 (M^+). Anal. Calcd for $C_{18}H_{13}O_2Br$: C; 63.36 H; 3.84. Found: C; 63.19 H;3.90.

Endo-1- bromo-3,4-benzo-7-methyl-7-phenylbicyclo-2,5-dione(endo-1e).

Yield 4.0%; m.p. 148-149 °C ; colorless needles (from hexane-benzene); IR(KBr) 1681, 1284, 772, 709 cm^{-1}. NMR($CDCl_3$) δ 1.92 (s,3H) 3.14 (s,1H) 6.93-6.98 (m,5H) 7.42-7.46 (m,2H) 7.72-7.79 (m,2H) MS *m/e* 340 (M^+). Anal. Calcd for $C_{18}H_{13}O_2Br$: C; 63.36 H; 3.84. Found: C; 63.34 H;3.95.

Photoreaction of Homonaphthoquinone(1a-d) in the Presence of Triethylamine(TEA) and Diethylamine(DEA).

Irradiation of homonaphthoquinones (**1a-d**, 2.5mmol dm^{-3}) and 5 equiv. excess of TEA and DEA in various solvents was carried out under an atmosphere of nitrogen with a high pressure mercury lamp through a filter (>330nm) for 2h.

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 excess amine were evaporated and the reaction mixture was submitted for ^1H NMR analysis to determine the conversion of **1b** and the yield of the dimeric compound **2** by using an internal standard, 4-(chloromethyl)biphenyl. The reaction mixture was washed with benzene (5ml x 3) to leave the amine salt of hydrogen bromide (12 mg, 68%). The combined washing solution was evaporated and the residue was chromatographed on silica gel to give successively the unconsumed **1b** (11 mg, 22 %) and (±)-**2b** (7 mg, 22 %) with a mixture of hexane and benzene as an eluent, and *meso*-**2b** (6 mg, 19 %) and the second crop of amine salt (1 mg, 6 %) with a mixture of benzene and ether, and finally a considerable amount of intractable resinous material (10 mg) with methanol. Formation of such resinous unidentified products was also the case for the photoreaction in the presence of DEA and DMA. In conformity with this preparative work, HPLC analysis of the reaction mixture showed the presence of at least seven by-products eluted prior to the unconsumed **1b** and *meso*- and (±)-**2b**. Judging from the proposed mechanism in Scheme 1, some of these products may be owing to the 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 by careful chromatography on silica gel.

Meso-2,2'-bi-3-diphenylmethylene-2,3-dihydro-1,4-naphthoquinone (meso-2b).

M.p. 278-279°C. Pale yellow prisms. (from benzene-hexane) IR(KBr) ;1686, 1487, 1285, 1242, 1227, 982, 704 cm^{-1}.

^{1}H NMR(CD_3Cl) δ 4.38 (s,2H) 6.73-6.77 (m,4H) 7.04-7.08 (m,4H) 7.13-7.17(m,6H) 7.21-7.26(m,6H) 7.62-7.66(m,4H) 7.80-7.86 (m,4H).

^{13}C NMR($CDCl_3$) δ 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, 194.0. MS *m/e* 646(M^+). Anal. Calcd for $C_{46}H_{30}O_4$: C;85.43 H;4.68. Found: C; 85.43 H;4.84.

(±)-2,2'-bi-3-diphenylmethylene-2,3-dihydro-1,4-naphthoquinone ((±)-2b) .

M.p. 288-290°C. Pale yellow prisms (from benzene-hexane). IR(KBr) ;1694, 1589, 1488, 1281, 1245, 1157, 984, 703 cm^{-1}. NMR($CDCl_3$) δ 4.30 (s,2H) 7.03-7.06 (m,4H) 7.14-7.24 (m,10H) 7.28-7.34 (m,6H) 7.56-7.60 (m,4H) 7.74-7.81 (m,4H). MS *m/e* 646 (M^+). Anal. Calcd for $C_{46}H_{30}O_4$: C;85.43 H;4.68. Found : C; 85.53 H;4.84.

Meso-2,2'-bi-3-bis(p-tolyl)di-methylene-2,3-dihydro-1,4-naphthoquinone (meso-2a).

M.p. 290-292°C. Yellow prisms (from benzene-hexane). IR(KBr) ; 1688, 1588, 1289, 1239, 1225, 981, 728 cm^{-1}.

NMR($CDCl_3$) δ 2.25 (s,6H) 2.29 (s,6H) 4.41 (s,2H) 6.61 (d, $J_{AA'}$=7.91, 4H) 6.90-7.00 (m,8H) 7.02-7.08 (m,4H) 7.58-7.68 (m,4H) 7.75-7.82 (m,2H) 7.82-7.85 (m,2H) . Calcd for $C_{50}H_{38}O_4$: 702.28. Found ; HR MS *m/e* 702.28.

(±)-2,2'-bi-3-di-p-tolylmethylene-2,3-dihydro-1,4-naphthoquinone ((±)-2a).

M.p. 287-289°C . Yellow prisms (from hexane-benzene). IR(KBr) : 1693, 1589, 1504, 1247, 985, 816, 728 cm^{-1}.

NMR($CDCl_3$) δ 2.25 (s,6H) 2.33 (s,6H) 4.34 (s,2H) 6.91 (d, $J_{AA'}$=8.25, 4H) 6.89-7.04 (m, 4H) 7.07-7.10 (m,8H) 7.56-7.88 (m,4H) 7.76-7.79 (m,4H). MS *m/e* 702(M^+). Anal. Calcd for $C_{50}H_{38}O_4$: C; 85.44 H; 5.45. Found: C; 85.07 H; 5.45.

Photoreaction of Homonaphthoquinone (1b) in the Presence of *N,N*-dimethylaniline (DMA).

Similar photoreaction of **1b** and 5 equiv. of DMA in acetonitrile gave the dimeric compound **2b**, 1:1 amine adduct **4** and amine salt. After irradiation, the reaction mixture was submitted for ^1H NMR analysis to determine the conversion of **1b** and the yield of products as described above. The reaction mixture was washed with benzene (5ml x 3) to leave the amine salt of hydrogen bromide. The combined washing solution was evaporated and the residue was chromatographed on silica gel to give successively unconsumed **1b** (12 mg, 24%), amine adduct **4** (4 mg ,10.7%), (±)-**2b** (5 mg, 18.4%) and with a mixture of hexane and benzene as an eluent ,and *meso*-**2b** (4 mg, 14.7%) with a mixture of benzene and ether, and finally an intractable resinous material (7mg) with methanol .

2-(p-dimethylamino)phenyl-3-diphenylmethylene-2-hydro-1,4-naphthoquinone (4).

M.p. 122-123°C. Yellow prisms (from hexane-benzene). IR(KBr): 1688, 1515, 1284, 1249, 1232, 1213, 701, 680 cm^{-1}.

^1H NMR(CD_3Cl) δ 2.90 (s,6H) 5.06 (s,1H) 6.63 (d, $J_{AA'}$=8.60, 2H) 7.02-7.13 (m,4H) 7.15-7.42 (m,8H) 7.63-7.70 (m,2H) 7.93-8.06 (m,2H).

^{13}C NMR($CDCl_3$) δ 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, 195.13 . HR MS Calcd for $C_{31}H_{25}NO_2$: 443.1887. Found : *m/e* 443.1882.

Photoreaction of 2-Bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone (3) in the Presence of Triethylamine (TEA).

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

Reductive Dimerization of 2-Bromo-3-diphenylmethylene-2,3-Dihydronaphthoquinone (3) to 2b with Zinc Powder.

To a stirred solution of **3** (100mg) in benzene (5 ml) was added zinc powder(100mg). After 1h, the solvent was evaporated and the reaction mixture was submitted for ^1H NMR analysis 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 an eluent, and ***meso*-2b** (10 mg, 12.5%) with a mixture of benzene and ether.

Photoreaction of Homonaphthoquinones (*exo*- and *endo*-1e) in the Presence of Triethylamine (TEA) in Acetonitrile

Photoreaction of ***exo*-** and ***endo*-1e** in the presence of TEA in acetonitrile or benzene gave the naphthofuran derivative **6** and 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 ml). After 2h irradiation, the reaction mixture was submitted for ^1H NMR analysis 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 (5ml x 3) to leave the amine salt of hydrogen bromide (11mg, 62%). The combined washing solution was evaporated and the residue was chromatographed on silica gel to give successively unconsumed **exo-1e** (11 mg, 22%), naphthofuran compound **3** (11 mg, 36.2%) with a mixture of hexane and benzene as an eluent, and a considerable amount of intractable resinous material (10 mg) with methanol.

5-Hydroxy-3-phenyl-naphtho[1,2-b]furan (6).

M.p. 116-117°C . Colorless needles(from hexane-benzene). IR(KBr) : 3407, 1595, 1449, 1247, 1067, 764, 697 cm^{-1}.

NMR($CDCl_3$) δ 5.17 (s,1H) 7.22 (s,1H) 7.36-7.41 (m,2H) 7.49-7.57 (m,3H) 7.62-7.68 (m,2H) 7.88 (s,1H) 8.25-8.31 (m,2H). ^{13}C NMR($CDCl_3$) δ 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, 148.0 . HR MS Calcd for $C_{18}H_{12}O_2$: 260.084 Found: *m/e* 260.086.

Photoreaction of Homonaphthoquinone (1b) in the Presence of Naphthalene, *o-,m-* and *p*-Dimethoxybenzenes and Triphenylamine in Polar Solvent.

Irradiation of homonaphthoquinone **1b** (6.2 mM) and an equiv. amount of naphthalene, dimethoxybenzenes, and triphenylamine in various solvents under an atmosphere of nitrogen for 2h with high pressure mercury lamp (>330nm) afforded 2-bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone (**3**) and 3,4-benzo-2-hydroxy-9-phenylxanthylium bromide (**7**).

The general procedure is represented for the case of **1b** (50.0mg) and *p*-dimethoxybenzene (17.1mg) in acetonitrile (20 ml). After irradiation, the reaction solution was submitted for UV analysis 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 submitted for ^1H NMR analysis to determine the yield of **3**(12.5%) as described above. The reaction mixture was washed with benzene (5ml x 4) to leave xanthlium salt **7** (6mg, 54.5% on 22% conversion). The combined washing solution was condensed and chromatographed on silica gel to give successively dimethoxybenzene (15mg), unconsumed **1b** (39mg, 78%) and 2-[hydroxy(diphenylmethyl)]-1,4-naphthoquinone **9** (1mg, 10.8%) with increasing amount of benzene in hexane (~100% by volume). The compound **9** was derived from hydrolysis of **3**.

3,4-Benzo-2-hydroxy-9-phenylxanthylium bromide(7). M.p. 283°C, dark red prisms; IR(KBr) 1622, 1601, 1489, 1414, 1377, 1270. UV(CH3CN); λ_{max}=240.4 nm (log ε=4.47) , 315.3 nm (4.26) , 395.0 nm (3.94), and 532.2 nm (3.70). ^1H NMR (CD_2Cl_2) δ 7.71-8.45 (m,12H) 8.64-8.68 (d, J=9.91,1H) 9.13-9.16 (d, J=8.58, 1H) 11.65 (s,1H) MS(Electrospray method) 323 (M-Br).

2-[Hydroxy(diphenyl)methyl]-1,4-naphthoquinone(9) .
M.p. 154-155°C Yellow prisms. IR(KBr) 3443, 1663, 1590, 1339, 1301, 1251, 755, 700 cm^{-1}. NMR($CDCl_3$) δ 5.10 (s,1H) 6.30 (s,1H) 7.30-7.37 (m,10H) 7.73-7.79 (m,2H) 8.02-8.09 (m,2H). MS *m/e* 340 (M^+). Anal. Calcd for $C_{23}H_{16}O_3$: C; 81.16 H; 4.74. Found: C; 80.96 H; 4.99.

Photoisomerization of 2-Bromo-3-diphenylmethylene-2,3-dihydronaphthoquinone (3).

Irradiation of a solution of **3** (100mg) in acetonitrile (5ml) for 24h furnished red prisms of **7** (69mg, 69%) on the glass surface. The filtrate was submitted for UV analysis 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** (100mg) in acetic acid (5 ml) was added zinc powder(100mg). After 2h, the solvent was evaporated and the reaction mixture was chromatographed on silica gel to give **8** (74.6% yield) with hexane-benzene as an eluent.

3,4-Benzo-2-hydroxy-9-phenylxanthene (8).

mp 161-162°C colorless needles IR(KBr) 3520, 1585, 1486, 1451, 1388, 1299, 1260, 1187, 754 cm^{-1}. ^{1}H NMR(CD_3Cl) 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) 8.05-8.08 (d, J=7.92, 1H) 8.40-8.43 (d, J=7.92,1H). ^{13}CNMR($CDCl_3$) δ 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, 150.8. MS *m/e*= 324 (M^+). Anal. Calcd for $C_{23}H_{16}O_2$: C; 85.16 H; 4.97. Found: C; 85.19 H; 5.18.

Photoreaction of Homonaphthoquinone (1b) in the Presence of Xanthene in Acetonitrile.

Irradiation of homonaphthoquinone **1b** (50 mg) and an equiv. amount of xanthene in acetonitrile (20 ml) for 2h with high pressure mercury lamp (>330nm) afforded the dimeric compound **2**, the ring-opened **3**, and xanthylium salt **7** along with 9,9'-bixanthenyl.

After irradiation, the reaction solution was submitted for UV analysis to determine the yield of **7** (38.7%) as described above. The solvent was evaporated and the reaction mixture was submitted for ^{1}H NMR analysis 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 (5ml x 4) to leave xanthlium salt **7** . The combined washing solution was condensed and chromatographed on silica gel to give successively 9,9'-bixanthenyl (2mg, 13.8%), unconsumed **1b** (34mg, 68%), **9** (1mg,7%), and the dimeric compound **2** (1mg,9%) with increasing amount of benzene in hexane (~100% by volume).

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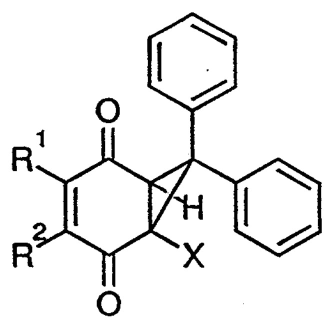
Chapter 2.

Photoinduced Electron-transfer Reactions of Homobenzoquinone

2-1 Introduction

As described in chapter 1, the irradiation of bromonaphthoquinone-fused diphenylcyclopropane (**1b**), so-called homonaphthoquinone, in the presence of alkylamine donors provides the dimer product (**2b**) and the hydrogen bromide salts of amines via an initial electron transfer from amine to the excited homoquinone. This photochemical reaction was dramatically changed to give xanthylium salt when the amines were replaced by arene donors. The crucial point differentiating the photoinduced degradation was rationalized by the nature of donor molecules, 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;[1,2,3] photoinduced hydrogen abstraction, photocycloaddition to olefins, and rearrangement.



1f; R^1=CH_3,R^2=H,X=Br
1g; R^1=CH_3,R^2=H, X=CH_3
1h; R^1=H,R^2=CH_3, X=CH_3
1i; R^1=R^2=CH_3, X=CH_3

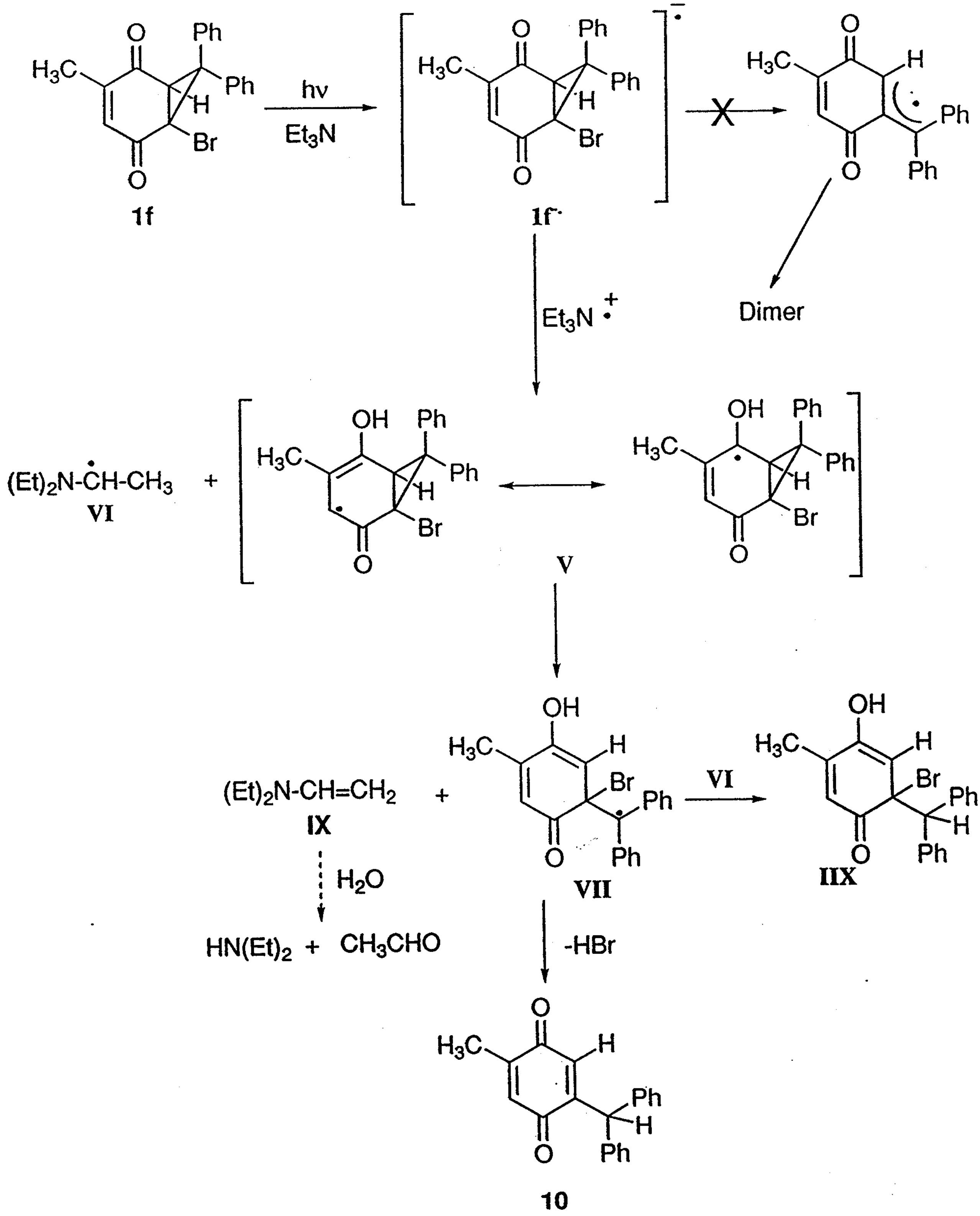
This paper deals with the photoinduced reaction of 2-bromo and 2-methyl-substituted diphenylhomobenzoquinones **1f-i** in the presence of triethylamine (TEA) and *N*,*N*-dimethylaniline (DMA). The aim of this study is to explore the scope of the photoreactions of homoquinones and the factors that determine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

2-2 Reactions of 2-bromo-5-methyl-homobenzoquinone

Irradiation of diphenylhomobenzoquinones (**1f**) and 5 equiv. excess of triethylamine(TEA) in benzene under an atmosphere of nitrogen with a high pressure mercury lamp through a filter (>330nm) for 2h gave the ring-opened hydrogenated product **10** (49.2%) together with the hydrogen bromide salts of the triethylamine (52.7%) and diethylamine (20.5 %) (Scheme 1).

Similarly, other alkyl amines, diethylamine, tri-*n*-propylamine, tri-*n*-butylamine, *N*,*N*-diethylaniline (DEAN) also provided quinone **10** (Table 1). The insufficient mass balance in these photoreactions would be owed to the further reaction of **10** under these photolytic conditions. Indeed, 2h's irradiation of **10** in the presence of 5 equiv. of TEA caused a considerable consumption of this quinone, although the reaction mixture was intractable.

However, when **1f** was irradiated in the presence of *N*,*N*-dimethylaniline (DMA) (for 2h, conversion; 56.9%), a substantial amount of 1:1 aminated adduct **11f** (31.5%) at the C=C double bond and 4,4'-methylenebis(N,N-dimetylaniline) **13** (16.0%) were obtained, together with **10** (9.5%) (Scheme 2). The structures of **10**, **11f**, and **13** were deduced on the basis of the IR, ^{1}H and ^{13}C NMR, and mass spectra. Stereochemistry of **11f** was determined by NMR analysis (*vide infra*).



Scheme 1

These reactions did not occur in the absence of amine or in the dark. Replacement of amine by a hydrogen donor 2-propanol also resulted in the quantitative recovery of **1f**. The fluorescence of **1f** (λ_{max}=420nm) were 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 **1f**. Free energy changes (ΔG) calculated according to the Weller equation for the system of **1f** and various amines used are all negative (Table 1). This means electron transfer from the amines to the excited **1f** 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 **1f** (1.0×10^{-3} mol dm^{-3}) and 5 to 20 equiv. of TEA.

Table 1 Photoreaction of homozenzoquinone (**1f**) with donors in benzene

Donor	ΔG kJ mol-1	Irrad. time/hour	Conv.(%)c	Yield(%)[b] 10
Triethylamine	-158	2	75.7	49.2
Triethylamine		0	0	0
None		2	0	0
Triphenylamine	-137	2	30.1	65.7
N,N-diethylaniline	-156	2	0	0
Diethylamine		2	27.9	23.9
Tri-n-propylamine		2	58.5	49.2
Tri-n-buthylamine		2	54.1	59.8
Naphthalene	-76	2	0	0

[a] Caluculated according to Weller equation; E_{0-0} of **1f** was measured to be 3.54 eV. Reduction potentioal of **1f** vs. SCE is -1.15 V in MeCN. [b] Due to the NMR peak areas of methine peak area of 4-(Chloromethyl)biphenyl used as an internal standard. [c] Caluculated on the consumed **1f**.

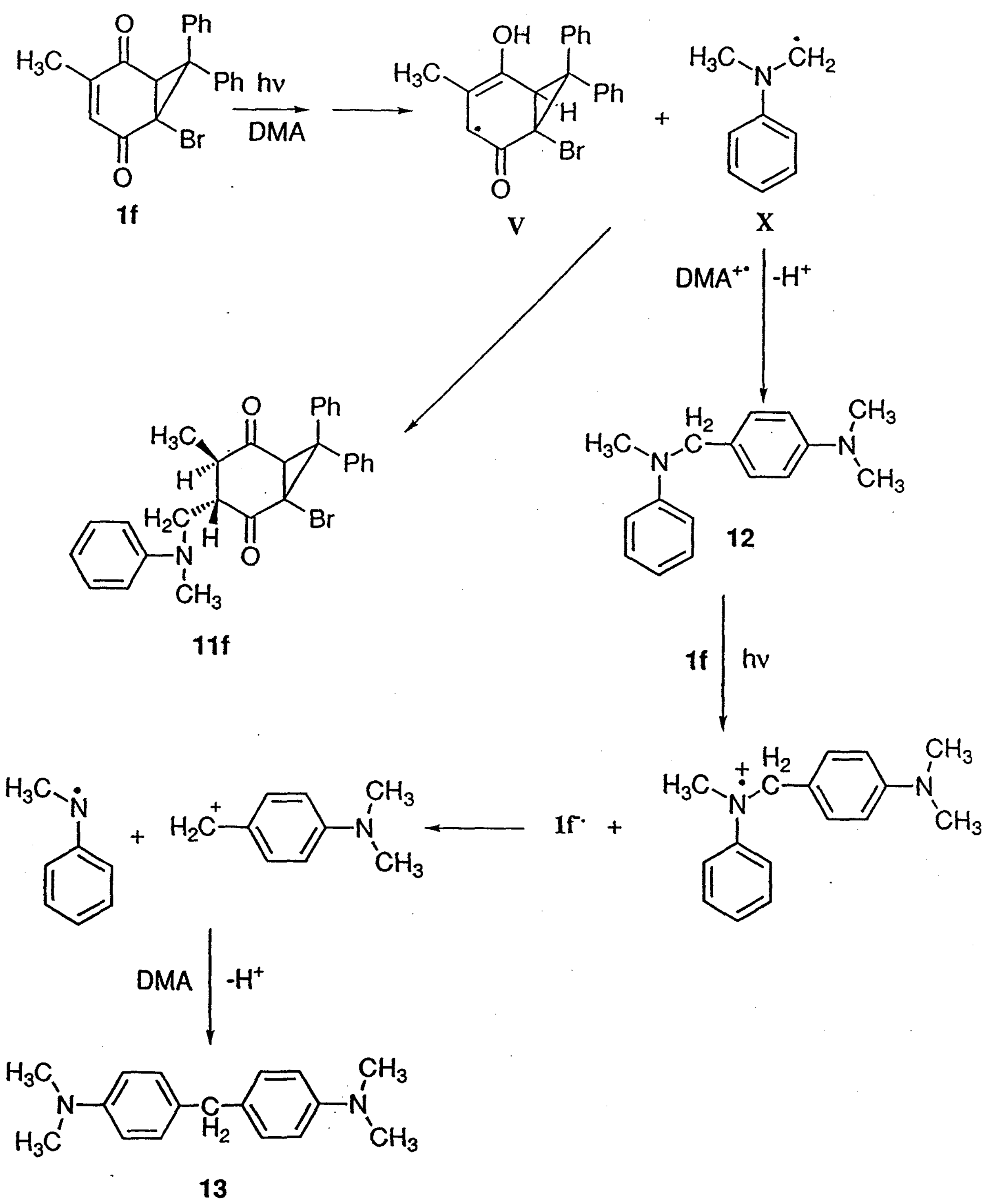
From these facts, we propose a possible mechanism for the representative reaction of **1f** with TEA as shown in Scheme 1. The first step is photoexcitation of **1f** followed by a single electron transfer (SET) from TEA to the excited **1f**. The radical anion **1f**$^{-\cdot}$ generated abstracts a proton from TEA$^{+\cdot}$ to be transformed into homobenzosemiquinone **V** and 1-(diethylamino)ethyl radical **VI** for TEA donor. The radical **V** undergoes β-fission to become **VII**. The radical **VII** leads to **10** by way of H abstraction from the amino radical **VI**, tautomerization and the loss of HBr. The resulting enamine **IX** easily hydrolyzed with residual water to degrade to diethylamine and acetaldehyde[5].

In the case of DMA donor, formation of aminated **11f** may be ascribed to the radical coupling of **V** with the counter metylphenylaminomethyl radical **X** as well as the tautomerization to keto-form(Scheme 2). This amino radical **X** is also participate in the formation of diamine **6**. Here, the radical **X** attacks DMA$^{+\cdot}$ at the *para*-position to give dimeric diamine **12** with loss of proton. The amine **12** will act as a donor component in the this photoreaction of **1f**. The diamine radical cation given by SET reaction dissociates into methylphenyl aminyl radical and *p*-dimethylaminobenzyl cation. The benzyl cation reacts further with the neutral DMA to afford **13**. Stoichiometrically, two protons can be extruded in the formation of one molecule of **13** as noted in Scheme 2. Such protons seem to be employed preferably in the neutralization of radical anion **1f**$^{-\cdot}$.

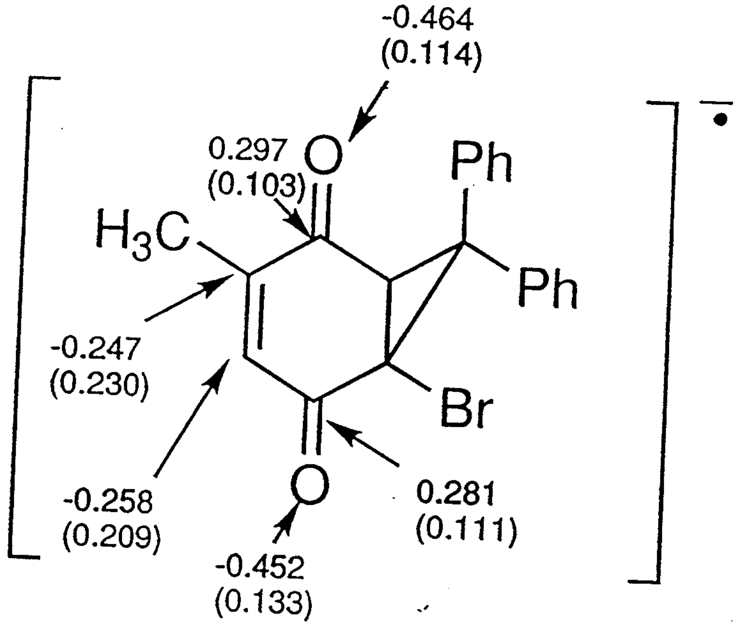
It is noteworthy that the DMA donor achieved radical coupling with **V** to give **11f**, but the alkyl amines such as TEA or *N,N*-diethylaniline (DEAN) did not provide the corresponding amine adduct. This difference mode of the reaction can be attributed to the bulkiness and hydrogen donating ability of the respective amino radicals. The amino radicals derived from TEA and DEAN are secondary and rather crowded around the radical center unfavorable for the coupling with **V**. Instead, these radicals are superior hydrogen donating species to facilitate the reducing process leading to **10**. However, DMA radical reverses the situation on account of the less sterical congestion and the poor hydrogen donation.

Of special interest is the marked difference in the products between the photoreaction of the present homobenzoquinone **1f** and that of the earlier homonaphthoquinone **1b**. As described chapter 1, reaction of **1b** in the presence of TEA provided isomeric mixture of dimer **2b** due to the coupling of the intermediary allyl radical (**II**). In the case of DMA donor, 1:1 amine adduct **4** associated with the cyclopropane ring-cleavage was obtained along with the dimer product.

If it were also true that the present homobenzoquinone **1f** follows the similar reaction course as did **1b**, 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 radical anion of **1f** is necessary to produce **10**, surpressing the possible process into the allyl radical. Why does the radical anion **1f**$^{-\cdot}$ derived from homobenzoquinone exhibit such a preferred proton acceptability? A comparison of molecular orbital calculations for both radical anions of **1b** and **1f** provided no satisfactory account for the preferential proton abstraction of **1a**$^{-\cdot}$ as judged from the almost comparable charge distribution on the quinone framework (Fig 1)*. Molecular orbital calculations by the PM3 method (ref 15) were performed with the MOPAC94 program using an CAChe system.



Scheme 2



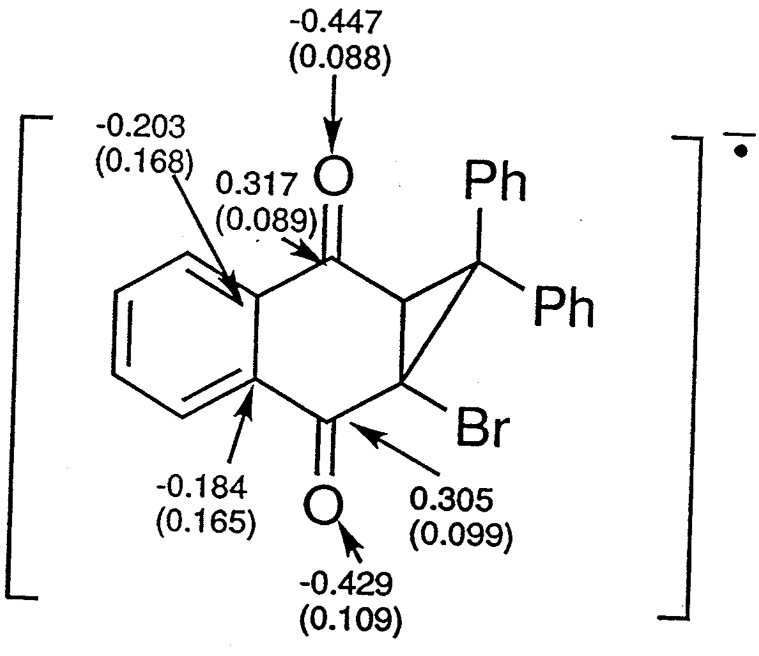
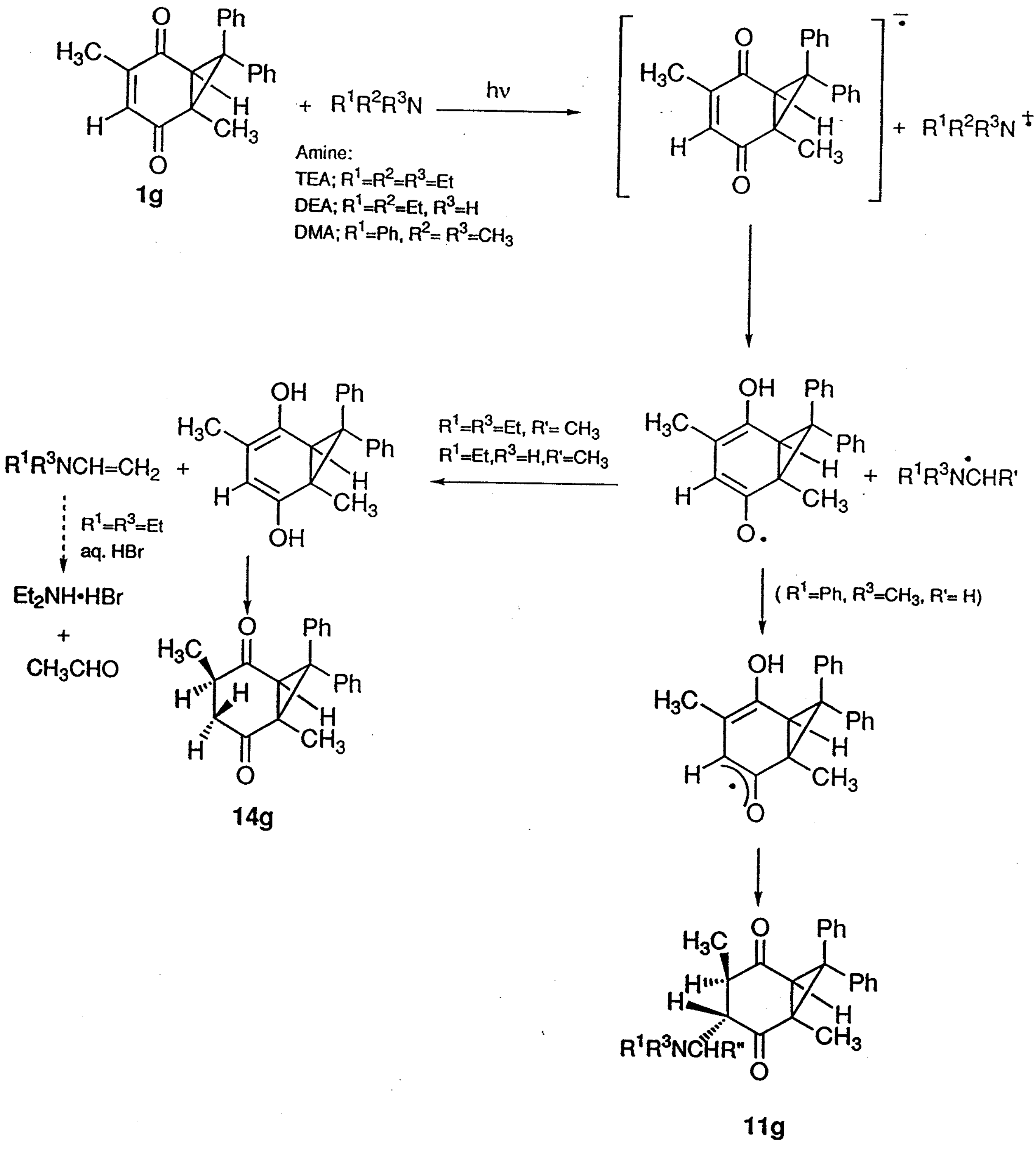


Fig. 1 Calculated charge distributions (upper) and spin density (lower) of radical anions of **1g** and **1 b**

It is also the same for the spin densities which will relate to the β-fission of cyclopropane ring to prepare allyl radical. Though inconsistent with the calculated distribution of the unpaired electron, we conceive that the fused-benzene nuclei of **1b**$^{-\cdot}$ may allow the accumulation of spin density on the adjacent ketyl carbon atom just as in π-conjugative benzyl radical, by which the β-fission is favored to give rise to the corresponding allyl radical. As for **1f**$^{-\cdot}$, one can easily imagine that the similar stabilization of the radical by allylic conjugation will cause the ring-opening of cyclopropane, but the spin densities of the terminal carbons of allyl radical is known to be lower than that of the benzyl radical[6]. The less liability of **1f**$^{-\cdot}$ 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 **1b**$^{-\cdot}$ and **1f**$^{-\cdot}$ requires further exploring experiments.

2-3 Reactions of 2,5-dimethyl-homobenzoquinone

Irradiation of di-, and trimethyl-substituted diphenylhomobenzoquinones **1g-i** and 5 equiv. excess of triethylamine (TEA), diethylamine (DEA) in benzene under an atmosphere of nitrogen with a high pressure mercury lamp through a short cut filter (>330 nm) for 5h gave the hydrogenated products **14g-i** in almost quantitative yields. In contrast, similar photoreaction of dimethyl-substituted **1g,h** in the presence of *N,N*-dimethylaniline(DMA) quantitatively provided the aminated products **11g,h**, though trimethyl-substituted **1i** substantially remained intact (Table 2 , Scheme 3). The structures of **11g,h** and **14g-i** were illustrated in Scheme 4.



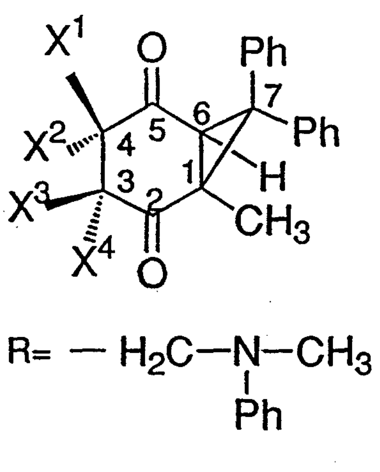
1g
hv
Amine:
TEA; R1=R2=R3=Et
DEA; R1=R2=Et, R3=H
DMA; R1=Ph, R2= R3=CH3
R1=R3=Et, R'= CH3
R1=Et,R3=H,R'=CH3
R1=R3=Et
aq. HBr
Et2NH•HBr
+
CH3CHO
14g
(R1=Ph, R3=CH3, R'= H)
11g

Scheme 3

Table 2 Photoreactions of homoquinones **1g,h,i** and **1d** with amines in benzene[a]

Entry	Homo-quinone	Donor (Additive)	Conv.(%)[b]	Yield.[c](%) 4	8
1	**1g**	TEA	100	—	~100(95)
2	**1g**	DEA	10.2	—	~100
3	**1g**	DMA	100	~100(83)	0
4	**1g**	Xanthene	7.4	0	0
5	**1g**	2-PrOH	3.6	0	0
6	**1h**	TEA	100	—	~100(72)
7	**1h**	DMA	100	~100(69)	0
8	**1i**	TEA	100	—	~100(70)
9	**1i**	DMA	4.2	0	0
10	**1d**	TEA	0	0	0
11	**1d**	DMA	0	0	0

[a] Irradiations were carried out on 8.3 mM of homoquinones in benzene (20ml) in the presence of 5 molar excess of donors for 5h with a 300W high-pressure Hg lamp. [b] Owing to the NMR peak areas of methine protons of **10** and of remaining **1**, **11** and **14** with respect to the methylene peak area of 4-(chloromethyl)biphenyl used as an internal standard. [c] Based on consumed **1**. [d] Carreid out in 2-PrOH.



11g; X^1=CH_3, X^2=X^3=H, X^4=R
11h; X^3=CH_3, X^1=X^4=H, X^2=R
14g; X^1=CH_3, X^2=X^3=X^4=H
14h; X^3=CH_3, X^1=X^2=X^4=H
14i; X^2=X^3=CH_3, X^1=X^4=H

Scheme 4

The stereochemistry of **11g,h** and **14g-i** were deduced by the NMR coupling constants between the protons at 3 and 4-positions, as represented in the case of **14**. The **14g** shows two doublet-doublet peaks at δ 1.12 (J_1=17.16, J_2=13.86Hz) and 2.34 (J_1=17.16, J_2=6.60Hz) ppm due to the geminal and vicinal couplings of the methylene at 3-position. The high field signal would be assigned to the shielded *syn*-proton and the low-field signal the *anti*-one with respect to the fused diphenylcyclopropane ring. The large vicinal coupling constant (J=13.86Hz) of the *syn*-proton suggests the *axial-axial* arrangement with the adjacent methine proton at 4-position. Indeed, X-ray crystal structure showed the half-chair comformation with a torsion angle; C(2)-C(3)-C(4)-C(5), -36° (Fig 2). In contrast, the small coupling constant (J=6.60Hz) of the *anti*-proton can be explained by the *axial-equatrial* arrangement. Similarly, structure of **14h** was determined. In case of **14i**, the geminal coupling constant J=6.60Hz is consistent with the *axial-equatrial* or *equatrial-equatrial* arrangement, but abnormally high field 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 **11g,h** 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 bulky amino group is rationalized by the favored *anti* attack of amino radical to the homobenzosemiquinone (vide infra). A careful NMR analysis of the reaction mixture showed stereoselective formation of **11** and **14**, with their possible stereoisomer being not detected.

The fluorescence of **1g** 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 **1g**. 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 **1g,h,i** (5mM) and 5 to 20 eq. excess of TEA or DMA. The photoreactions of **1g,h,i** did not occur in the absence of amine or in the dark. In place of amine, use of xanthene or 2-propanol as a hydrogen source resulted in almost the quantitative recovery of **1g** (92.6 and 96.4%) without any detection of hydrogenated **14g**. Furthermore, benzo-fusion of homobenzoquinone framework endowed it with persistency for photo-hydrogenation and amination as tested for methyl-substituted homonaphthoquinone **1d**.

Keeping these facts, we can outline the following mechanism for the photohydrogenation and amination of **1g,h,i** (Scheme 3).

The first step is photoexcitation of **1g,h,i** followed by single electron transfer from the amine donor to the excited **1g,h,i**. The generated radical anion **1g**$^{-\bullet}$ abstracts a proton from the radical cation of amine to give homobenzosemiquinone **V** and amine radical **VI** or **X**. Here, the hydrogen donating ability of amine radical plays a decisive role in the subsequent degradation of **V**. Hydrogen abstraction is an exclusive process for **VI** arising from TEA and DEA to provide **14g,h,i** by way of diketalization. Thus, the dealkylation of amine can be rationalized by hydrolysis of resulting vinyl amine. Absence of such labile hydrogen results in the radical coupling to afford amine adduct **11g,h**, as in the case of DMA. A preliminary experiment showed that the compound **14g** undergo complete deuterium exchange at the 3- and 4-positions, while **11g** at only 4-position when treated with methanol-*d4* under the influence of a few drops of TEA or DMA for 5h in dark. This finding is consistent with occurrence of keto-enolization of **11** and **14**, strongly supporting 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 **1g** 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). Photoamination of trimethyl-substituted **1i** with DMA did not occur probably because of the steric hindrance around the relevant C=C double bond. The radical **V** of **1i** would return the H atom to the amine radical.

Fig 2 X-Ray crystal analysis of **11g**

ANISOTROPIC THERMAL PARAMETERS

Atom	U11	U22	U33	U12	U13	U23
O(1)	0.066(1)	0.052(1)	0.080(1)	-0.017(1)	0.014(1)	-0.019(1)
O(2)	0.076(1)	0.049(1)	0.100(2)	-0.017(1)	0.016(1)	0.010(1)
C(1)	0.0315(7)	0.0402(9)	0.0450(10)	0.0006(7)	0.0000(7)	-.0021(8)
C(2)	0.0424(9)	0.0433(11)	0.0504(11)	-.0017(8)	0.0023(8)	-.0048(9)
C(3)	0.046(1)	0.053(1)	0.067(2)	0.003(1)	0.018(1)	-0.005(1)
C(4)	0.042(1)	0.062(2)	0.056(1)	0.000(1)	0.011(1)	0.005(1)
C(5)	0.0420(9)	0.0433(12)	0.0614(13)	-.0006(8)	0.0036(9)	0.0100(9)
C(6)	0.0391(8)	0.0358(9)	0.0514(11)	0.0045(7)	0.0011(7)	0.0025(8)
C(7)	0.0322(7)	0.0307(8)	0.0488(10)	0.0009(6)	-.0006(7)	-.0011(7)
C(8)	0.0294(7)	0.0734(16)	0.0536(12)	-.0044(9)	0.0015(7)	0.0006(11)
C(9)	0.050(1)	0.088(3)	0.094(3)	0.001(1)	0.026(2)	0.024(2)
C(10)	0.0389(8)	0.0413(11)	0.0443(10)	0.0065(7)	-.0021(7)	-.0046(8)
C(11)	0.101(3)	0.047(1)	0.063(2)	0.021(1)	0.004(2)	-0.006(1)
C(12)	0.144(5)	0.066(2)	0.060(2)	0.043(3)	0.011(2)	-0.009(2)
C(13)	0.087(2)	0.106(3)	0.046(1)	0.047(2)	0.004(1)	-0.011(2)
C(14)	0.051(1)	0.090(2)	0.044(1)	0.004(1)	0.000(1)	-0.004(1)
C(15)	0.0437(9)	0.0551(13)	0.0489(11)	-.0020(9)	0.0000(8)	-.0049(10)
C(16)	0.0314(7)	0.0353(9)	0.0524(11)	0.0034(7)	-.0016(7)	0.0002(7)
C(17)	0.042(1)	0.035(1)	0.080(2)	0.001(1)	-0.003(1)	0.005(1)
C(18)	0.054(1)	0.047(1)	0.111(3)	0.014(1)	-0.007(2)	0.015(2)
C(19)	0.042(1)	0.067(2)	0.104(3)	0.013(1)	-0.013(1)	0.007(2)
C(20)	0.038(1)	0.063(2)	0.080(2)	-0.004(1)	-0.011(1)	0.000(1)
C(21)	0.039(1)	0.044(1)	0.062(1)	-0.006(1)	-0.009(1)	-0.001(1)

$$T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+U_{12}hka^*b^*+U_{23}klb^*c^*+U_{13}hla^*c^*)]$$

FRACTIONAL ATOMIC COORDINATES & U(iso)

Atom	x/a	y/b	z/c	U(iso)
O(1)	0.9667(3)	0.4727(1)	0.6955(4)	0.067
O(2)	0.7183(4)	0.2646(1)	0.6329(5)	0.076
C(1)	0.9684(2)	0.3864(1)	0.5495(3)	0.039
C(2)	0.9002(3)	0.4295(1)	0.6541(3)	0.046
C(3)	0.7465(3)	0.4188(1)	0.7101(4)	0.056
C(4)	0.7078(3)	0.3573(1)	0.7492(4)	0.054
C(5)	0.7672(3)	0.3130(1)	0.6383(4)	0.049
C(6)	0.8969(2)	0.3272(1)	0.5419(3)	0.042
C(7)	0.8736(2)	0.3656(1)	0.3894(3)	0.038
C(8)	1.1372(2)	0.3913(1)	0.5487(3)	0.052
C(9)	0.5384(4)	0.3501(2)	0.7624(7)	0.078
C(10)	0.9555(2)	0.3486(1)	0.2430(3)	0.042
C(11)	0.9602(6)	0.2917(2)	0.1942(5)	0.071
C(12)	1.0342(8)	0.2767(2)	0.0574(5)	0.091
C(13)	1.0993(5)	0.3170(2)	-0.0342(4)	0.080
C(14)	1.0925(3)	0.3736(2)	0.0113(4)	0.062
C(15)	1.0206(3)	0.3896(1)	0.1483(3)	0.050
C(16)	0.7222(2)	0.3914(1)	0.3317(3)	0.040
C(17)	0.7089(3)	0.4491(1)	0.2948(4)	0.053
C(18)	0.5689(4)	0.4719(2)	0.2354(6)	0.071
C(19)	0.4422(3)	0.4374(2)	0.2145(6)	0.072
C(20)	0.4548(3)	0.3798(2)	0.2488(5)	0.061
C(21)	0.5945(3)	0.3567(1)	0.3069(4)	0.049
H(3A)	0.67239	0.43188	0.62293	0.08(2)
H(3B)	0.73899	0.44098	0.80903	0.07(1)
H(4)	0.74810	0.34941	0.86236	0.09(2)
H(6)	0.95934	0.29388	0.54050	0.036(7)
H(8A)	1.19622	0.40431	0.64853	0.07(1)
H(8B)	1.15492	0.41721	0.46063	0.08(2)
H(8C)	1.17412	0.35431	0.52313	0.10(2)
H(9A)	0.51411	0.31143	0.78719	0.10(2)
H(9B)	0.48301	0.36103	0.65819	0.11(3)
H(9C)	0.50971	0.37443	0.84929	0.09(2)
H(11)	0.91233	0.26289	0.25459	0.10(2)
H(12)	1.03990	0.23730	0.02662	0.15(4)
H(13)	1.14934	0.30613	-0.12892	0.08(2)
H(14)	1.13779	0.40213	-0.05253	0.07(1)
H(15)	1.01549	0.42910	0.17798	0.09(2)
H(17)	0.79595	0.47326	0.31047	0.05(1)
H(18)	0.56044	0.51166	0.20837	0.09(2)
H(19)	0.34552	0.45347	0.17689	0.10(2)
H(20)	0.36752	0.35567	0.23198	0.06(1)
H(21)	0.60311	0.31671	0.33034	0.05(1)

INTRAMOLECULAR BOND ANGLES

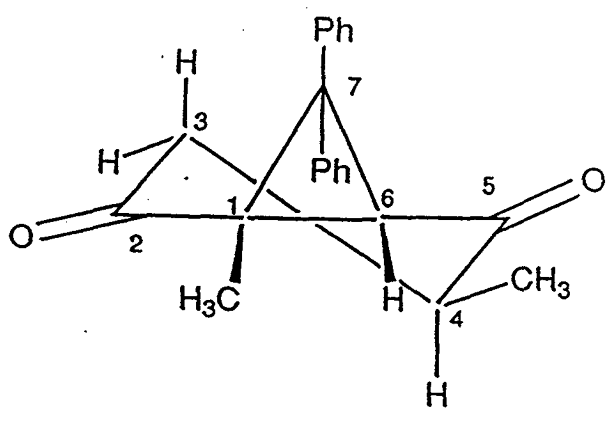
Minimum bond length= 0.90A : Maximum bond length= 1.65A

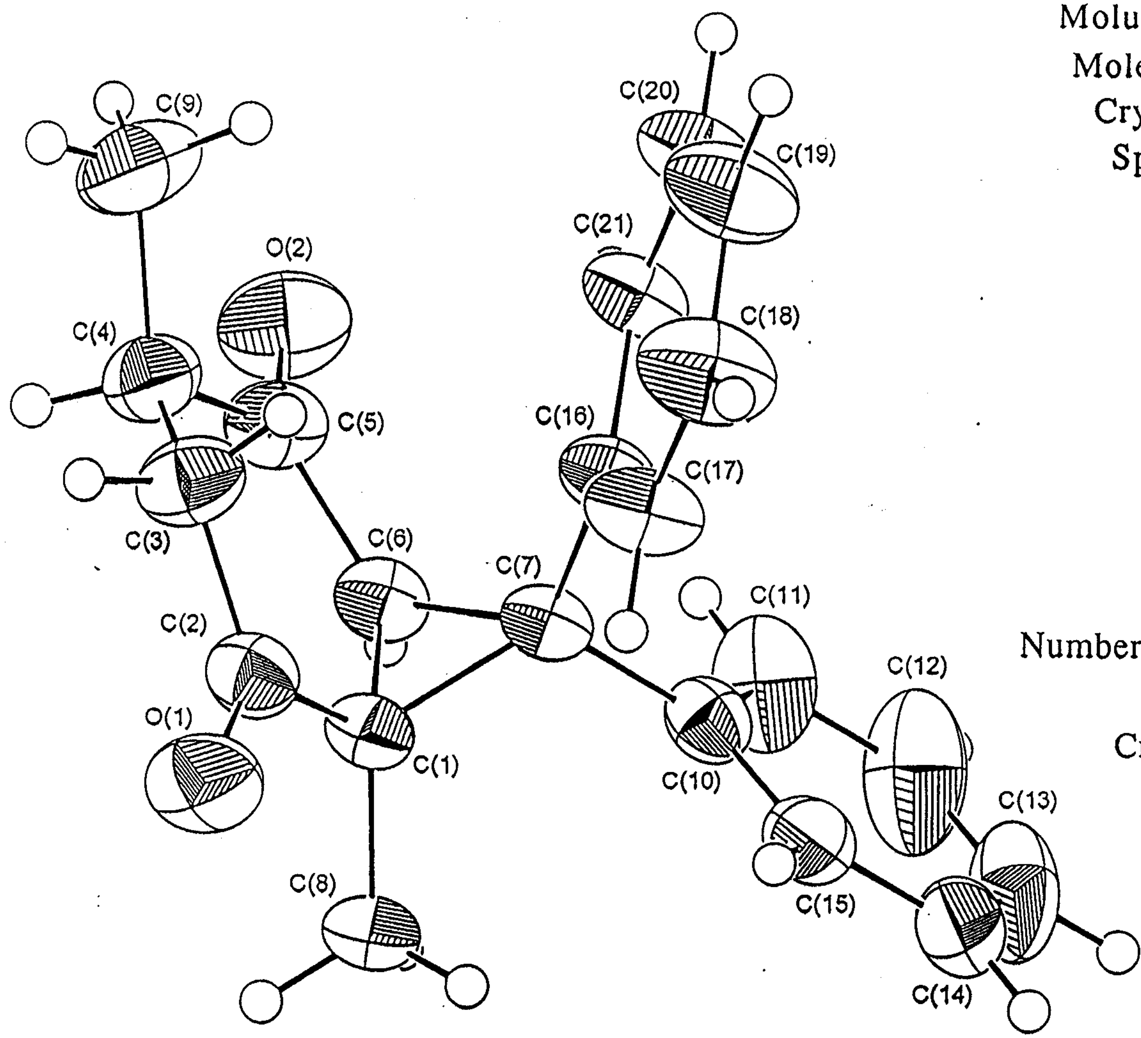
C(2)-C(1)-C(6)	116.5(2)	C(2)-C(1)-C(7)	117.9(2)
C(2)-C(1)-C(8)	114.8(3)	C(6)-C(1)-C(7)	59.4(2)
C(6)-C(1)-C(8)	118.8(2)	C(7)-C(1)-C(8)	118.4(2)
O(1)-C(2)-C(1)	120.6(3)	O(1)-C(2)-C(3)	119.6(3)
C(1)-C(2)-C(3)	119.7(3)	C(2)-C(3)-C(4)	116.9(3)
C(2)-C(3)-H(3A)	107.6(3)	C(2)-C(3)-H(3B)	107.8(3)
C(4)-C(3)-H(3A)	107.5(3)	C(4)-C(3)-H(3B)	107.8(3)
H(3A)-C(3)-H(3B)	109.1(3)	C(3)-C(4)-C(5)	115.5(3)
C(3)-C(4)-C(9)	111.4(3)	C(3)-C(4)-H(4)	108.0(3)
C(5)-C(4)-C(9)	112.3(3)	C(5)-C(4)-H(4)	108.0(3)
C(9)-C(4)-H(4)	100.4(3)	O(2)-C(5)-C(4)	121.3(3)
O(2)-C(5)-C(6)	118.9(3)	C(4)-C(5)-C(6)	119.7(3)
C(1)-C(6)-C(5)	121.6(3)	C(1)-C(6)-C(7)	60.7(2)
C(1)-C(6)-H(6)	120.1(2)	C(5)-C(6)-C(7)	120.4(2)
C(5)-C(6)-H(6)	107.9(3)	C(7)-C(6)-H(6)	120.1(3)
C(1)-C(7)-C(6)	59.9(2)	C(1)-C(7)-C(10)	118.0(2)
C(1)-C(7)-C(16)	121.4(2)	C(6)-C(7)-C(10)	116.1(2)
C(6)-C(7)-C(16)	121.7(2)	C(10)-C(7)-C(16)	111.2(2)
C(1)-C(8)-H(8A)	118.4(3)	C(1)-C(8)-H(8B)	107.3(3)
C(1)-C(8)-H(8C)	107.3(3)	H(8A)-C(8)-H(8B)	107.3(3)
H(8A)-C(8)-H(8C)	107.3(3)	H(8B)-C(8)-H(8C)	109.0(3)
C(4)-C(9)-H(9A)	111.4(4)	C(4)-C(9)-H(9B)	109.0(4)
C(4)-C(9)-H(9C)	109.2(4)	H(9A)-C(9)-H(9B)	109.1(5)
H(9A)-C(9)-H(9C)	109.1(5)	H(9B)-C(9)-H(9C)	109.0(5)
C(7)-C(10)-C(11)	120.4(3)	C(7)-C(10)-C(15)	120.8(3)
C(11)-C(10)-C(15)	118.7(3)	C(10)-C(11)-C(12)	119.8(4)
C(10)-C(11)-H(11)	120.2(4)	C(12)-C(11)-H(11)	120.0(4)
C(11)-C(12)-C(13)	121.3(5)	C(11)-C(12)-H(12)	119.4(5)
C(13)-C(12)-H(12)	119.3(6)	C(12)-C(13)-C(14)	119.3(4)
C(12)-C(13)-H(13)	120.4(6)	C(14)-C(13)-H(13)	120.3(5)
C(13)-C(14)-C(15)	120.6(4)	C(13)-C(14)-H(14)	119.7(4)
C(15)-C(14)-H(14)	119.7(4)	C(10)-C(15)-C(14)	120.4(3)
C(10)-C(15)-H(15)	119.8(3)	C(14)-C(15)-H(15)	119.9(3)
C(7)-C(16)-C(17)	120.7(2)	C(7)-C(16)-C(21)	120.0(2)
C(17)-C(16)-C(21)	119.2(3)	C(16)-C(17)-C(18)	120.0(3)
C(16)-C(17)-H(17)	120.0(3)	C(18)-C(17)-H(17)	120.0(3)
C(17)-C(18)-C(19)	120.3(4)	C(17)-C(18)-H(18)	119.8(4)
C(19)-C(18)-H(18)	119.9(4)	C(18)-C(19)-C(20)	120.0(4)
C(18)-C(19)-H(19)	120.1(4)	C(20)-C(19)-H(19)	119.9(4)
C(19)-C(20)-C(21)	119.9(3)	C(19)-C(20)-H(20)	120.1(3)
C(21)-C(20)-H(20)	120.0(4)	C(16)-C(21)-C(20)	120.5(3)
C(16)-C(21)-H(21)	119.7(3)	C(20)-C(21)-H(21)	119.7(3)

INTRAMOLECULAR BOND LENGTHS

Minimum bond length= 0.90A : Maximum bond length= 1.65A

O(1)-C(2)	1.202(4)	O(2)-C(5)	1.217(4)
C(1)-C(2)	1.490(4)	C(1)-C(6)	1.527(4)
C(1)-C(7)	1.540(4)	C(1)-C(8)	1.512(3)
C(2)-C(3)	1.512(4)	C(3)-C(4)	1.525(5)
C(3)-H(3A)	0.960(4)	C(3)-H(3B)	0.960(4)
C(4)-C(5)	1.505(5)	C(4)-C(9)	1.537(5)
C(4)-H(4)	0.960(4)	C(5)-C(6)	1.501(4)
C(6)-C(7)	1.519(4)	C(6)-H(6)	0.961(3)
C(7)-C(10)	1.508(4)	C(7)-C(16)	1.506(3)
C(8)-H(8A)	0.960(3)	C(8)-H(8B)	0.960(3)
C(8)-H(8C)	0.960(4)	C(9)-H(9A)	0.960(6)
C(9)-H(9B)	0.960(5)	C(9)-H(9C)	0.959(6)
C(10)-C(11)	1.395(5)	C(10)-C(15)	1.394(4)
C(11)-C(12)	1.390(7)	C(11)-H(11)	0.960(4)
C(12)-C(13)	1.369(8)	C(12)-H(12)	0.961(5)
C(13)-C(14)	1.382(8)	C(13)-H(13)	0.960(5)
C(14)-C(15)	1.388(5)	C(14)-H(14)	0.960(4)
C(15)-H(15)	0.960(3)	C(16)-C(17)	1.389(4)
C(16)-C(21)	1.397(4)	C(17)-C(18)	1.394(5)
C(17)-H(17)	0.960(3)	C(18)-C(19)	1.386(5)
C(18)-H(18)	0.961(4)	C(19)-C(20)	1.382(6)
C(19)-H(19)	0.960(4)	C(20)-C(21)	1.392(4)
C(20)-H(20)	0.960(3)	C(21)-H(21)	0.959(3)





Molucular formula	$C_{21}H_{20}O_2$
Molecular weight	304.4
Crystal system	Monoclinic
Space group	P 21/a
a	8.925(4)A
b	23.48(1)A
c	8.049(3)A
β	96.36(3) degrees
V	1676(1)A^3
Z	4
Dm	1.21 g/cm^3
Dx	1.20 g/cm^3
μ(CuKα)	λ=0.71073
Number of reflections	4531
R	0.0699
Crystal size	0.5*0.35*0.30 mm^3

2-4 Conclusion

Photoreactions of diphenylhomobenzoquinones **1f-i** 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-bromosubstituted diphenylhomobenzoquinone **1f** with triethylamine (TEA) resulted in the ring-opening of fused-cyclopropane moiety to give 2-diphenylmethyl-1,4-benzoquinone (**10**). However, photoreaction of **1f** with *N,N*-dimethylaniline (DMA) yielded the 1:1 aminated bicyclic dione **11f** and bis(*p*-dimethylaminophenyl)methane (**7**) along with **10**. By contrast, irradiation of 1-methyl substituted diphenylhomobenzoquinones **1g-i** with TEA brought about the hydrogenation of the C=C double bond to give bicyclic diones **14g-i**. Similar photoreaction of **1g,h** with DMA provided only the 1:1 aminated bicyclic diones **11g,h**, although trimethyl substituted **1i** essentially remained intact.

2-5 Experimental

All melting points were taken on a Yanagimoto micro-melting point apparatus and were uncorrected. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL EX-270 MHz instrument with Me_4Si(δ 0.00) as an internal standard. IR, ultraviolet 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 300W high pressure Hg lamp, and the short cut filter used were an Eikohsha glass filter FT-3 (>330nm).

Materials. Benzene were refluxed over lithium aluminium hydride for 1 day and fractionated. All amine and arene donors were commercial origin and were purified by distillation after drying over NaOH for liquid donors or by recrystallization for solid ones. Diarylhomobenzoquinones (**1f-i**) 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[5].

Photoreaction of Bromo-substituted Homonaphthoquinone (1f) in the Presence of Triethylamine (TEA), Diethylamine (DEA), tri-n-Propylamine, tri-n-Butylamine and N,N-Diethylaniline.
Irradiation of homonaphthoquinones (**1f**, 2.5mmol dm^{-3}) and 5 equiv. excess of amines in benzene was carried out under an atmosphere of nitrogen with a high pressure mercury lamp through a filter (>330nm) for 2h.

The general procedure is represented for the case of **1f** (50.0 mg) and TEA (76.3 mg) in benzene (20 ml). After irradiation, the solvent and excess amine were evaporated and the reaction mixture was submitted for ^{1}H NMR analysis to determine the conversion of **1f** and the yield of the hydrogenated compound **10** by using an internal standard, 4-(chloromethyl)biphenyl. The reaction mixture was washed with benzene (5ml x 3) to leave the amine salt of hydrogen bromide (7 mg). The combined washing solution was evaporated and the residue was chromatographed on silica gel to give successively the unconsumed **1f** (10 mg, 20%) and **10** (14 mg, 45%) with a mixture of hexane and benzene as an eluent, and finally a considerable amount of intractable resinous material (7 mg) with methanol. Formation of such unidentified resinous products was also the case for the 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 **1f** and **10**. On the basis of the proposed mechanism in Scheme 1, some of these products may be owing to the side pathway via some radicals and the amino radical, and also the further photodegradation of these primary adducts. However, we could not isolate them by careful chromatography on silica gel.

5-Methyl-2-diphenylmethyl-1,4-benzoquinone (10).

mp 150-150.8 °C, yellow prisms (from benzene-hexane)

υ_{max}(KBr) 1646, 1613, 1261, 1262, 1166 and 748.

δ_H($CDCl_3$) 7.36 - 7.10 (m, 10H), 6.33 (d, J = 1.65Hz, 1H)

6.26 (d, J = 1.65, 1H), 5.61 (s, 1H) 2.04 (d, J = 1.65, 3H).

HR MS m/e calcd for: 288.11508; found: 288.1154.

Found: C; 83.37, H; 5.74; Calcd for $C_{20}H_{16}O_2$: C; 83.31, H; 5.59.

Photoreaction of Homobenzoquinone (1f) in the Presence of N,N-Dimethylaniline (DMA).

Similar photoreaction of **1f** and 5 equiv. of DMA in benzene gave **10** and 1:1 amine adduct **11f**, bis(*p*-dimethylaminophenyl)-methane **13** and amine salt. After irradiation, the reaction mixture was washed with benzene (5ml x 3) to leave the amine salt of hydrogen bromide. The combined washing solution was evaporated and the residue was chromatographed on silica gel to give successively unconsumed **1f** (24 mg, 43.1%), **10** (3 mg , 9.5%), **11f** (10 mg, 31.5%) and with a mixture of hexane and benzene as an eluent, and bis(*p*-dimethylaminophenyl)methane **13** (3mg, 16%)

with a mixture of benzene and ether, and finally an intractable resinous material (15 mg) with methanol . The structure of **13** was confirmed by a comparison of its IR, NMR spectra with those of the authentic specimen[7].

r-1,c-3,t-4-1-Bromo-3-(methyl)phenylaminomethyl-4-methyl-7,7-diphenylbicyclo[4.1.0]hepta-2,5-dione(11f).

m.p. 112-114 °C. Colorless prisms(from benzene-hexane). υ_{max}(KBr) 1669, 1447, 749 and 710. δ_H($CDCl_3$) 6.9-7.4(m,12H), 6.70(t(J=7.26 Hz),1H), 6.43(d(J=7.92), 2H), 3.60(dd(J_1=14.52, J_2=7.26 Hz), 1H) ,3.47(s,1H), 3.40(dd(J_1=14.52, J_2=3.30 Hz), 1H), 2.86(s,3H), 2.33(qd(J_1=6.60, J_2=12.87 Hz),1H) 1.66(ddd(J_1=7.26, J_2=3.30, J_3=12.87Hz),1H), 1.55(s,3H) 1.02(d(J=6.60 Hz), 3H).

HR MS m/e calcd for: 487.112; found: 487.115. Found: C; 69.05, H; 5.49, N; 2.95; Calcd for $C_{28}H_{26}NO_2Br$: C; 68.86, H; 5.36, N; 2.87.

*Photoreaction of Methyl-substituted Homobenzoquinone (**1g,h,i**) in the Presence of Triethylamine (TEA).*

The general procedure is represented for the case of dimethyl-substituted homobenzoquinone **1g** (50.0mg) and TEA (83.1mg) in benzene(20ml). After irradiation, the solvent and volatile matters were distilled in vacuo and collected in a chilled trap (-78°C). The residue was submitted for ^{1}H NMR analysis to determine the yield of **14g** as well as the conversion of **1f** by using an internal standard. The compound **14g** (48mg, 95%) was isolated by column chromatography on silica gel with benzene as an eluent. The distillate was treated with a few drops of hydrobromic acid and dried in vacuo to give 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 hydrolyzed to diethylamine and acetaldehyde[9]. In case of high-boiling DMA, similar column chromatographic treatment of the reaction mixture containing amine yielded the recovered DMA (25mg) with hexane and the aminated **11g** (58mg, 83%) with benzene.

trans-1,4-Dimethyl-7,7-diphenylbicyclo[4.1.0]hepta-2,5-dione (14g).

m.p. 178-179°C. Colorless prisms (from benzene-hexane).

υ_{max}(KBr) 1687, 1447, 1312, 1208, 752 and 712.

δ_H($CDCl_3$) 7.2-7.5 (m,10H), 2.88 (s, 1H), 2.58 (ddq(J_1=13.86, J_2=6.60, J_3=6.60 Hz), 1H), 2.34 (dd(J_1=17.16, J_2=6.60 Hz),1H), 1.21 (s,3H) 1.12 (dd(J_1=17.16, J_2=13.86Hz),1H),0.81 (d(J=6.60 Hz), 3H). MS[EI] m/e =304 (M^+)

Found: C; 82.68, H; 6.73; Calcd for $C_{21}H_{20}O_2$: C; 82.86, H; 6.62.

trans-1,3-Dimethyl-7,7-diphenylbicyclo[4.1.0]hepta-2,5-dione(14h).

m.p. 103-104°C. Colorless prisms (from benzene-hexane).

υ_{max}(KBr) 1688, 1446, 1304, 1268, 1042, 709 and 681.

δ_H($CDCl_3$) 7.1-7.4 (m,10H), 2.81 (d(J=1.98 Hz), 1H), 2.59 (ddq(J_1=13.53, J_2=6.60, J_3=6.60 Hz), 1H), 2.28 (ddd(J_1=16.50, J_2=6.60, J_3=1.98 Hz),1H), 1.17 (s,3H), 1.04 (dd(J_1=16.50, J_2=13.50Hz),1H), 0.85 (d(J=6.60 Hz), 3H).

$\delta^{13}C$($CDCl_3$) 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, 14.7. MS[EI] m/e =304 (M^+).

Found: C; 82.83, H; 6.67; Calcd for $C_{21}H_{20}O_2$: C; 82.86, H; 6.62.

r-1,t-3,c-4-1,3,4-Trimethyl-7,7-diphenylbicyclo[4.1.0]hepta-2,5-dione(14i).

m.p. 161-162°C. Colorless prisms (from benzene-hexane).

υ_{max}(KBr) 1701, 1446, 1233, 751, 711 and 700.

δ_H($CDCl_3$) 7.1-7.5 (m,10H), 3.00 (q,d(J1=7.59, J2=6.60 Hz), 1H) 2.82 (q,d(J1=7.58, J2=6.60 Hz),1H), 2.76 (s,1H), 1.21 (s,3H) 0.56 d(J=7.59 Hz), 3H), 0.17 (d(J=7.60 Hz), 3H).MS[EI] m/e =318 (M+).
Found: C; 82.83, H; 6.67; Calcd for $C_{22}H_{22}O_2$: C; 82.99, H; 6.96.

r-1,c-3,t-1-1,4-Dimethyl-3-methylphenylaminomethyl-7,7-diphenylbicyclo[4.1.0]hepta-2,5-dione (11g).

m.p. 128-129 °C. Yellow prisms (from benzene-hexane).

υ_{max}(KBr) 1685, 1502, 1446, 1190 and 748 .

δ_H($CDCl_3$) 6.9-7.4 (m,12H), 6.67 (t(J=7.26 Hz),1H), 6.45 (d(J=8.58 Hz), 2H), 3.65 (dd(J_1=14.85, J_2=7.26 Hz), 1H), 3.19 (dd(J_1=14.85, J_2=3.30 Hz), 1H), 2.87 (s,1H), 2.78 (s,3H), 2.30 (qd(J_1=12.53, J_2=6.27 Hz),1H), 1.62 (ddd(J_1=12.53, J_2=7.26, J_3=3.30Hz),1H), 1.18 (s,3H), 1.01 (d(J=6.27 Hz), 3H). MS[EI] m/e =423 (M^+)
Found: C; 82.03, H; 6.93, N; 3.29; Calcd for $C_{29}H_{29}O_2N$: C; 82.24, H; 6.90, N; 3.31.

r-1,t-3,c-4-1,3-Dimethyl-4-methylphenylaminomethyl-7,7-diphenylbicyclo[4.1.0]hepta-2,5-dione (11h).

m.p. 140-141 °C. Colorless prisms (from benzene-hexane).

υ_{max}(KBr)1685, 1599, 1501, 1208, 748, 709 and 694.

δ_H($CDCl_3$) 6.9-7.4 (m,12H), 6.67 (t(J=7.26 Hz),1H), 6.46 (d(J=7.91), 2H), 3.60 (dd(J_1=14.52, J_2=7.26 Hz), 1H), 3.26 (dd(J_1=14.52, J_2=3.30 Hz), 1H), 2.94 (s,1H), 2.79 (s,3H), 2.33 (qd(J_1=6.60, J_2=12.21 Hz),1H)

1.66 (ddd(J_1=7.26, J_2=3.30, J_3=12.21Hz),1H), 1.21 (s,3H), 0.96 (d(J=6.60 Hz), 3H). MS[EI] m/e =423 (M^+).

Found: C; 81.28, H;6.84, N;3.28; Calcd for $C_{29}H_{29}O_2N$: C; 81.24, H; 6.90, N; 3.31.

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Chapter 3.

Intramolecular photoinduced electrn-transfer reactions of homonaphthoquinone

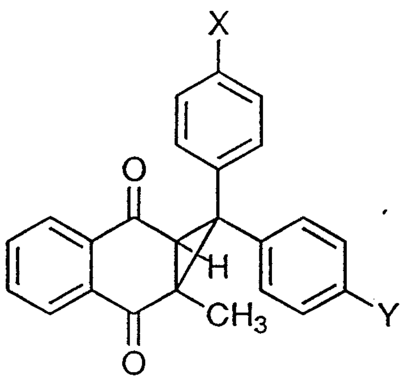
3-1 Introduction

Intramolecular photoinduced electron-transfer (PET) systems[1] are useful and important means in relevance to artificial photosynthesis[2] and molecular-level optoelectronics[3]. Intensive studies have been made of a variety of covalently-linked donor -acceptor (D-A) molecules to understand the structural and photophysical factors governing electron-transfer *i.e.*, the D-A distance and orientation, the free energy of reaction, and the electronic coupling[4]. However, there are only a few examples of dynamic electron-transfer reactions involving bond-cleavage and bond-forming processes, such as photofragmentation of 1,2-diamine linked acceptors[5] and photocyclization of styrylamines[6] and photoelimination of aminoacetophenone[7].

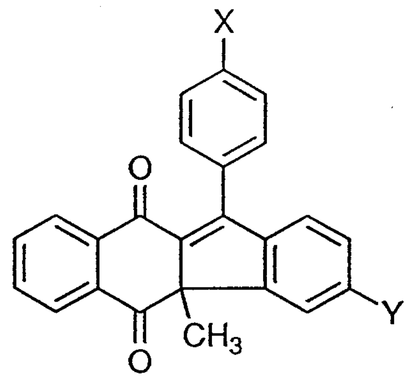
As described in chapter 1 and 2, the intermolecular PET reactions of homonaphthoquinones, with various donors[8,9] proceed through a bond-cleavage of the strained cyclopropane ring releasing bromide ion gave dimeric products and xanthylium ion depending on the donor used. The present chapter deals with a new photoreaction of homonaphthoquinones *via* the intramolecular PET. For this purpose, anisyl-linked homonaphthoquinones, **1j,k** were employed.

3-2 Photoinduced Electron-transfer Reactions of Donor-substituted homonaphthoquinone

Irradiation of bis(p-anisyl)homonaphthoquinone **1j** under the influence of 5 molar equiv. of $Mg(ClO_4)_2$ in acetonitrile through the pyrex filter (>330 nm) with a high pressure mercury lamp for 1 day provided indenonaphthoquinone **15a** in almost quantitative yield (Table 1).



1j; X=Y=OCH_3
endo-**1k**; X=OCH_3, Y=H
exo-**1k**; X=H, Y=OCH_3
1l; X=Y=CH_3



15a; X=Y=OCH_3
15b; X=OCH_3, Y=H
15c; X=H, Y=OCH_3

Table 1 Photoreaction of homonaphthoquinone **1j,k** in the presence of $Mg(ClO_4)_2$ in acetonitrile

Entry	Homonaphtho quionone	Irrad. time(day)	Conv.(%)[a]	Yield(%)[a] 15a	15b
1	**1j**	1	100	~100	——
2	**1j**	3	100	~100	——
3	**1j**	1	0	0	——
4	**endo-1k**	3	45.1[b]	——	93.5
5	**exo-1k**	3	37.2[c]	——	83.1
6	**endo-1k**	3	0[d]	——	0
7	**1l**	3	0	——	——
8	**1d**	3	0	——	——

a Measured from NMR areas of methyl protons of remaining of **1k** and **15b** to the methylene peak of 4-chloromethylbiphenyl used as an internal standard. b Unconsumed **1k** consist of 78/22 (*endo*/*exo*) mixture. c Unconsumed **1k** consist of 25/75 (*endo*/*exo*) mixture. d Unconsumed **1k** consist of 81/19 (*endo*/*exo*) mixture.

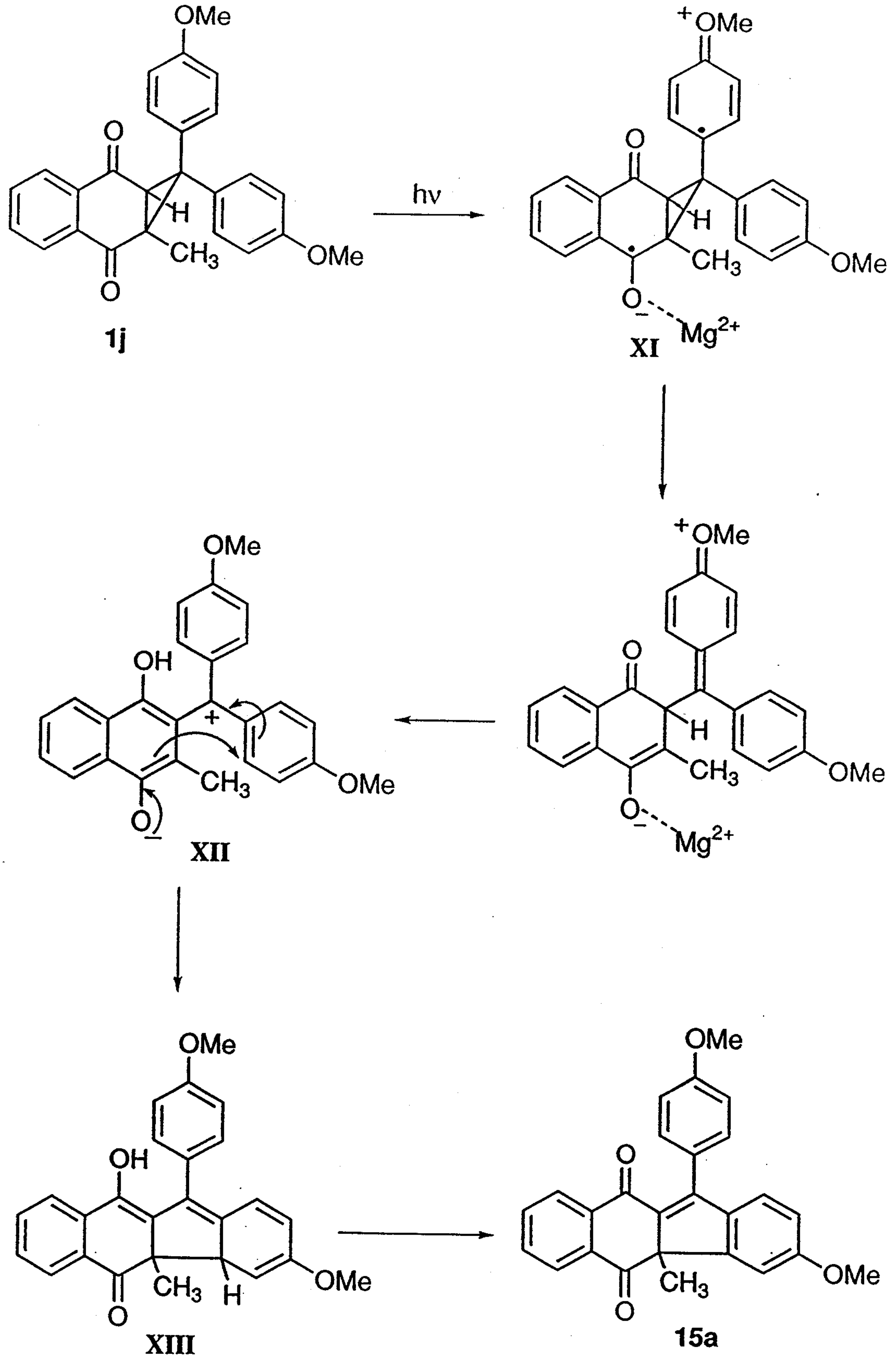
Similar reaction of *p*-anisylphenylhomonaphthoquinones (*endo*- and *exo*-**1k**) gave indenonaphthoquinone **15b** as sole product accompanied by the *endo-exo* photoisomerization of **1k** (entry 4,5). The possible constitutional isomer **15c** could not be detected by careful ^{1}H NMR analysis. The structures of **15a,b** were deduced by IR, ^{1}H NMR, ^{13}C NMR and mass spectra as well as X-ray crystal analysis for **15b**.

The general work-up procedure is represented for the case of **1j** (50mg) with 5 equiv. of $Mg(ClO_4)_2$ (140 mg) in acetonitrile (20 ml). After irradiation, the solvent was evaporated and the reaction mixture was submitted for ^{1}H NMR analysis to determine the yield of **15a**. The product **15a** was extracted with benzene (10 ml x 2) from the aqueous solution of the reaction mixture, and the organic layer was dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel to give **15a** (41mg, 82%) with a mixture of hexane and benzene as an eluent.

Photoreaction of **1j** even in the presence of 0.1 molar equiv. of $Mg(ClO_4)_2$ also gave **15a** in quantitative yield (entry 2). These reactions did not occur in the absence of $Mg(ClO_4)_2$ or in the dark at ordinary temprature (entry 3,6). Furthermore, it was noted that the replacement of anisyl group of **1j** by tolyl or phenyl endowed it with photopersistency as experienced for bis(*p*-tolyl)-(**1l**) and diphenyl-homonaphthoquinones (**1d**) (entry 7,8).

The absorption spectrum of the methoxy-substituted **1j** was very similar to that of the unsubstituted **1d**, and appreciable intramolecular CT absorption was not observed. Fluorescence of **1j** and **1d** were observed in acetonitrile with irradiation light of 300 nm at which **1j** and **1d** have almost the same logarithmic molar absorptivity, 3.26 and 3.24. Homonaphthoquinone **1j** showed a strong fluorescence (λ_{max}=502.6nm), but the fluorescence of **1d** was negligible. The emission maximum of **1j** shifted to shorter wavelength with the decreasing solvent polarity *i.e.*, 453.8 (THF) and 413.4 nm (benzene). The fluorescence of **1j** would be due to the formation of intramolecular exciplex of **1j**[6]. Therefore, the present reaction can be envisaged as involving an intramolecular PET from the anisyl group to the naphthoquinone moiety under the influence of $Mg(ClO_4)_2$.

Keeping these observations, it is proposed that the present photoreaction proceeds through a mechanism outlined for **1j** (Scheme 1). The first step is photoexcitation of **1j** followed by an intramolecular electron transfer. The generated radical ion **XI** undergoes ring-opening to lead to a zwitter ion **XII**. Here, the role of added $Mg(ClO_4)_2$ is probably suppression of the intramolecular back-electron transfer as well as stabilization of **XI**. Such additive effects of metal ions to enhance the PET reaction is well-known[8,9]. Next step is an intramolecular cyclization of **XII** as rationalized by the nucleophilic attack of the enolate ion moiety to the *ortho*-position of the benzyl cation to afford tetracyclic quinol **XIII**. Furthermore, the resulting **XIII** may be oxidised into aromatized indenonaphthoquinone **15a**. Absence of possible **15c** in the photoreaction of **1k** would be due to the unfavorable electron accumulation on the anisyl ring. Thus, the chemoselective formation of **15b** both for *endo*- and *exo*-**1k** are not surprising since the stereochemistry of **1k** would be completely lost in the zwitterion intermediate like **XII**. It is noteworthy that the conversion of *endo*-**1k** was higher than that of *exo*-**1k** (entry 4,5). This would owe to the more enhanced intramolecular Coulomb interaction for the *endo*-radical ion **XI** than the *exo*-one[10].


OMe
O
H
CH3
O
OMe
1j
hν
+OMe
O
H
CH3
O
Mg2+
OMe
XI
+OMe
O
H
CH3
O
Mg2+
OMe
OMe
OH
+
CH3
O
OMe
XII
OMe
OH
CH3
H
O
OMe
XIII
OMe
O
CH3
O
OMe
15a

Scheme 1

Fig 1 X-Ray crystal analysis of **15b**

ANISOTROPIC THERMAL PARAMETERS

Atom	U11	U22	U33	U12	U13	U23
O(1)	0.088(2)	0.054(1)	0.066(2)	-0.001(1)	0.030(1)	0.012(1)
O(2)	0.074(2)	0.052(1)	0.071(2)	-0.004(1)	0.011(1)	0.008(1)
O(3)	0.058(2)	0.087(2)	0.107(2)	0.004(2)	-0.005(2)	0.044(2)
C(4)	0.048(2)	0.045(2)	0.041(2)	0.002(1)	0.008(1)	-0.002(1)
C(5)	0.050(2)	0.038(1)	0.038(1)	0.001(1)	0.006(1)	-0.001(1)
C(6)	0.047(2)	0.048(2)	0.055(2)	0.001(1)	0.011(1)	0.002(2)
C(7)	0.056(2)	0.043(2)	0.044(2)	0.003(1)	0.007(1)	0.000(1)
C(8)	0.044(2)	0.040(1)	0.039(1)	0.001(1)	0.003(1)	0.000(1)
C(9)	0.049(2)	0.046(2)	0.047(2)	0.001(1)	0.008(1)	0.005(1)
C(10)	0.043(2)	0.048(2)	0.039(2)	-0.004(1)	0.003(1)	0.002(1)
C(11)	0.047(2)	0.052(2)	0.043(2)	-0.002(1)	0.005(1)	-0.004(1)
C(12)	0.050(2)	0.047(2)	0.045(2)	-0.009(1)	0.005(1)	0.002(1)
C(13)	0.058(2)	0.051(2)	0.043(2)	0.001(2)	0.013(1)	-0.002(1)
C(14)	0.054(2)	0.041(2)	0.060(2)	0.004(1)	0.009(2)	0.006(2)
C(15)	0.047(2)	0.046(2)	0.046(2)	0.001(1)	0.013(1)	0.002(1)
C(16)	0.046(2)	0.065(2)	0.053(2)	0.006(2)	0.003(1)	-0.005(2)
C(17)	0.049(2)	0.067(2)	0.046(2)	-0.005(2)	0.016(1)	-0.006(2)
C(18)	0.054(2)	0.056(2)	0.045(2)	-0.003(2)	0.019(1)	0.000(2)
C(19)	0.069(2)	0.062(2)	0.049(2)	0.016(2)	-0.001(2)	0.006(2)
C(20)	0.043(2)	0.070(2)	0.048(2)	0.002(2)	0.010(1)	-0.006(2)
C(21)	0.049(2)	0.080(3)	0.064(2)	0.005(2)	0.013(2)	-0.004(2)
C(22)	0.063(2)	0.053(2)	0.046(2)	0.009(2)	0.011(2)	0.006(2)
C(23)	0.049(2)	0.061(2)	0.058(2)	0.004(2)	0.009(2)	0.010(2)
C(24)	0.062(2)	0.065(2)	0.055(2)	0.005(2)	0.018(2)	-0.007(2)
C(25)	0.044(2)	0.112(4)	0.072(3)	-0.001(2)	0.009(2)	-0.014(3)
C(26)	0.063(2)	0.081(3)	0.064(2)	-0.016(2)	0.020(2)	-0.004(2)
C(27)	0.103(4)	0.064(3)	0.071(3)	-0.008(3)	0.045(3)	0.007(2)
C(28)	0.057(2)	0.108(4)	0.077(3)	-0.028(3)	0.018(2)	-0.010(3)

$$T=\exp[-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+U_{12}hka^*b^*+U_{23}klb^*c^*+U_{13}hla^*c^*)]$$

FRACTIONAL ATOMIC COORDINATES & U(iso)

Atom	x/a	y/b	z/c	U(iso)
O(1)	0.36662(17)	0.67319(17)	-0.16082(36)	0.071
O(2)	0.17819(17)	0.22556(17)	0.57399(37)	0.067
O(3)	0.11033(16)	0.53323(21)	0.21546(45)	0.086
C(4)	0.29959(19)	0.36246(21)	0.62774(41)	0.046
C(5)	0.33932(18)	0.40943(19)	0.51176(39)	0.043
C(6)	0.27667(19)	0.60198(23)	0.20958(46)	0.051
C(7)	0.3486(2)	0.4784(2)	0.1221(4)	0.049
C(8)	0.27864(17)	0.45879(20)	0.37941(39)	0.042
C(9)	0.20461(19)	0.44251(21)	0.41374(43)	0.049
C(10)	0.30095(18)	0.51364(21)	0.23450(40)	0.045
C(11)	0.4234(2)	0.4073(2)	0.5368(4)	0.049
C(12)	0.34698(19)	0.61577(22)	-0.03512(42)	0.049
C(13)	0.3717(2)	0.5286(2)	-0.0130(4)	0.052
C(14)	0.3000(2)	0.6530(2)	0.0768(5)	0.053
C(15)	0.21021(19)	0.38081(21)	0.57526(43)	0.048
C(16)	0.4671(2)	0.3576(3)	0.6792(5)	0.056
C(17)	0.0763(2)	0.3180(3)	0.4011(4)	0.055
C(18)	0.1577(2)	0.2989(2)	0.5188(4)	0.053
C(19)	0.4270(2)	0.3108(3)	0.7924(5)	0.062
C(20)	0.05932(19)	0.39869(26)	0.31063(45)	0.055
C(21)	-0.0188(2)	0.4152(3)	0.2110(6)	0.066
C(22)	0.3433(2)	0.3127(2)	0.7686(5)	0.056
C(23)	0.1243(2)	0.4659(3)	0.3064(5)	0.057
C(24)	0.1781(3)	0.4261(3)	0.7320(5)	0.062
C(25)	-0.0783(2)	0.3522(4)	0.2029(6)	0.078
C(26)	0.0158(3)	0.2539(3)	0.3880(6)	0.071
C(27)	0.4122(3)	0.6380(3)	-0.2837(7)	0.082
C(28)	-0.0611(3)	0.2717(4)	0.2892(6)	0.082
H(6)	0.238(2)	0.631(2)	0.285(5)	0.06(1)
H(7)	0.3652(19)	0.4139(22)	0.1356(44)	0.052(9)
H(11)	0.453(2)	0.446(2)	0.464(5)	0.06(1)
H(13)	0.4092(19)	0.5015(24)	-0.0792(44)	0.06(1)
H(14)	0.278(2)	0.715(2)	0.062(5)	0.06(1)
H(16)	0.5259(19)	0.3523(21)	0.6928(41)	0.046(9)
H(19)	0.459(2)	0.275(2)	0.888(5)	0.07(1)
H(21)	-0.026(2)	0.468(2)	0.157(4)	0.05(1)
H(22)	0.315(2)	0.278(3)	0.845(5)	0.07(1)
H(24A)	0.119(2)	0.441(3)	0.693(5)	0.07(1)
H(24B)	0.186(2)	0.389(3)	0.841(5)	0.08(1)
H(24C)	0.208(2)	0.484(3)	0.763(5)	0.08(1)
H(25)	-0.132(2)	0.365(3)	0.138(5)	0.08(1)
H(26)	0.030(2)	0.198(3)	0.438(5)	0.07(1)
H(27A)	0.473(3)	0.613(3)	-0.218(6)	0.10(2)
H(27B)	0.387(2)	0.586(3)	-0.345(6)	0.08(1)
H(27C)	0.423(2)	0.689(3)	-0.354(5)	0.08(1)
H(28)	-0.104(3)	0.226(3)	0.281(6)	0.08(1)

INTRAMOLECULAR BOND LENGTHS

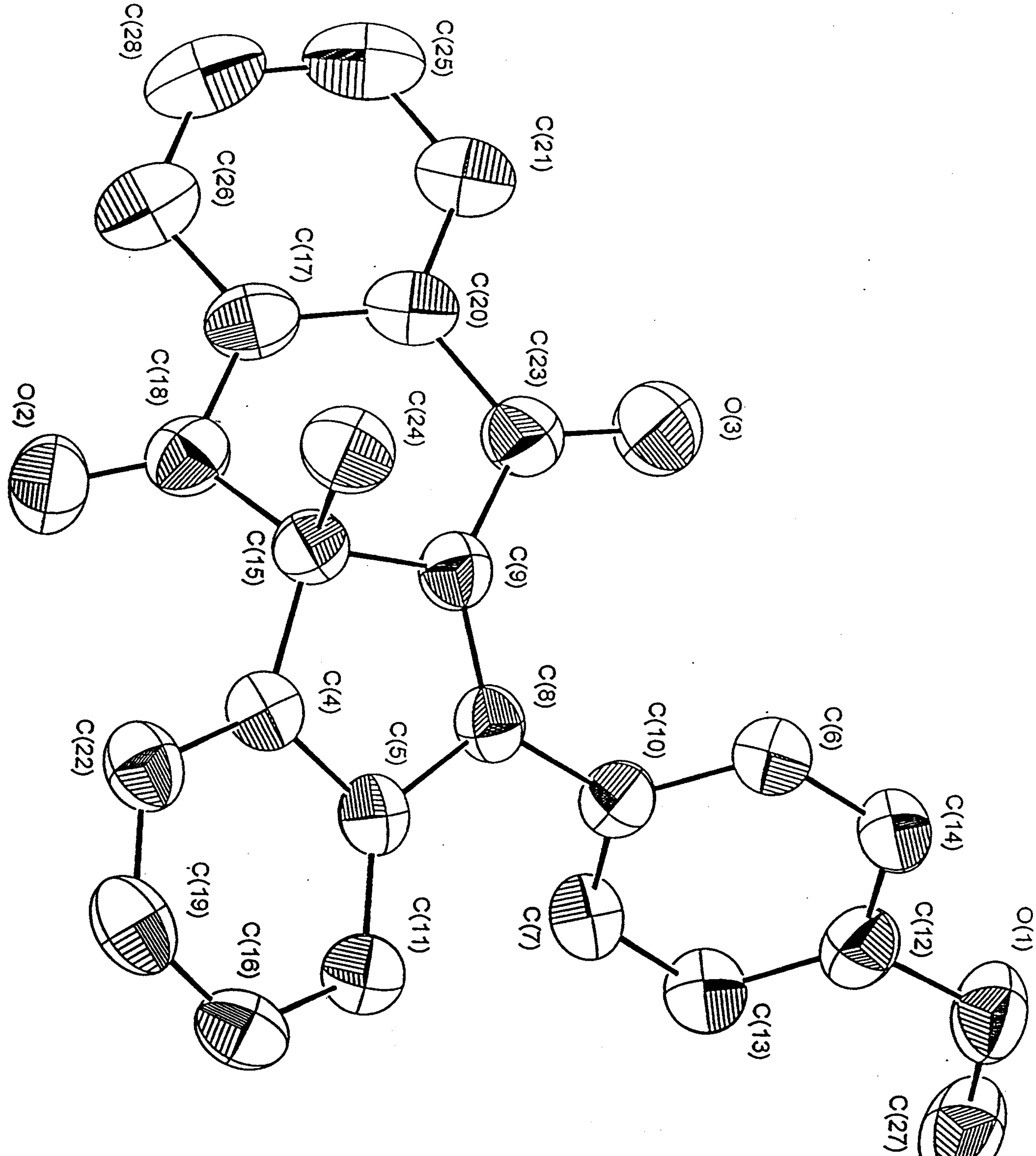
Minimum bond length= 0.85A :		Maximum bond length= 1.65A	
O(1)-C(12)	1.371(5)	O(1)-C(27)	1.419(6)
O(2)-C(18)	1.209(5)	O(3)-C(23)	1.221(5)
C(4)-C(5)	1.396(5)	C(4)-C(15)	1.504(5)
C(4)-C(22)	1.380(5)	C(5)-C(8)	1.474(5)
C(5)-C(11)	1.393(5)	C(6)-C(10)	1.397(5)
C(6)-C(14)	1.379(5)	C(6)-H(6)	1.04(4)
C(7)-C(10)	1.386(5)	C(7)-C(13)	1.384(5)
C(7)-H(7)	1.01(4)	C(8)-C(9)	1.349(5)
C(8)-C(10)	1.476(5)	C(9)-C(15)	1.516(5)
C(9)-C(23)	1.470(5)	C(11)-C(16)	1.388(5)
C(11)-H(11)	1.01(4)	C(12)-C(13)	1.381(5)
C(12)-C(14)	1.387(5)	C(13)-H(13)	0.97(4)
C(14)-H(14)	1.00(4)	C(15)-C(18)	1.530(5)
C(15)-C(24)	1.551(6)	C(16)-C(19)	1.384(6)
C(16)-H(16)	0.98(4)	C(17)-C(18)	1.501(5)
C(17)-C(20)	1.396(6)	C(17)-C(26)	1.396(6)
C(19)-C(22)	1.388(6)	C(19)-H(19)	0.97(4)
C(20)-C(21)	1.398(5)	C(20)-C(23)	1.500(5)
C(21)-C(25)	1.376(7)	C(21)-H(21)	0.89(4)
C(22)-H(22)	0.97(4)	C(24)-H(24A)	1.01(4)
C(24)-H(24B)	0.98(5)	C(24)-H(24C)	1.02(5)
C(25)-C(28)	1.380(8)	C(25)-H(25)	0.96(4)
C(26)-C(28)	1.383(7)	C(26)-H(26)	0.94(4)
C(27)-H(27A)	1.11(5)	C(27)-H(27B)	0.96(5)
C(27)-H(27C)	0.97(5)	C(28)-H(28)	0.99(5)

Molucular formula	$C_{25}H_{18}O_3$
Molecular weight	366
Crystal system	Monoclinic
Space group	P 21/c
a	16.874(9)A
b	15.108(7)A
c	7.500(6)A
β	101.83(6) degrees
V	1871(1)A^3
Z	4
Dm	1.25 g/cm^3
Dx	1.26 g/cm^3
μ(CuKα)	λ=0.71073
Number of reflections	5146
R	0.0471
Crystal size	0.35*0.30*0.25 mm^3

INTRAMOLECULAR BOND ANGLES

Minimum bond length= 0.85A : Maximum bond length= 1.65A

C(12)-O(1)-C(27)	116.7(3)	C(5)-C(4)-C(15)	109.1(3)
C(5)-C(4)-C(22)	120.3(3)	C(15)-C(4)-C(22)	130.6(3)
C(4)-C(5)-C(8)	108.7(3)	C(4)-C(5)-C(11)	120.7(3)
C(8)-C(5)-C(11)	130.5(3)	C(10)-C(6)-C(14)	120.8(3)
C(10)-C(6)-H(6)	122.1(20)	C(14)-C(6)-H(6)	117.1(20)
C(10)-C(7)-C(13)	121.3(4)	C(10)-C(7)-H(7)	119.5(19)
C(13)-C(7)-H(7)	119.1(19)	C(5)-C(8)-C(9)	108.8(3)
C(5)-C(8)-C(10)	122.2(3)	C(9)-C(8)-C(10)	129.0(3)
C(8)-C(9)-C(15)	110.9(3)	C(8)-C(9)-C(23)	129.6(3)
C(15)-C(9)-C(23)	119.0(3)	C(6)-C(10)-C(7)	118.5(3)
C(6)-C(10)-C(8)	121.5(3)	C(7)-C(10)-C(8)	120.0(3)
C(5)-C(11)-C(16)	118.8(4)	C(5)-C(11)-H(11)	121.6(20)
C(16)-C(11)-H(11)	119.2(20)	O(1)-C(12)-C(13)	125.2(3)
O(1)-C(12)-C(14)	114.1(3)	C(13)-C(12)-C(14)	120.7(4)
C(7)-C(13)-C(12)	119.2(4)	C(7)-C(13)-H(13)	117.0(21)
C(12)-C(13)-H(13)	123.5(21)	C(6)-C(14)-C(12)	119.6(4)
C(6)-C(14)-H(14)	116.9(20)	C(12)-C(14)-H(14)	123.4(20)
C(4)-C(15)-C(9)	102.5(3)	C(4)-C(15)-C(18)	114.6(3)
C(4)-C(15)-C(24)	111.7(3)	C(9)-C(15)-C(18)	109.8(3)
C(9)-C(15)-C(24)	111.1(3)	C(18)-C(15)-C(24)	107.1(3)
C(11)-C(16)-C(19)	120.0(4)	C(11)-C(16)-H(16)	119.5(19)
C(19)-C(16)-H(16)	120.4(19)	C(18)-C(17)-C(20)	121.7(4)
C(18)-C(17)-C(26)	118.4(4)	C(20)-C(17)-C(26)	119.9(4)
O(2)-C(18)-C(15)	122.6(4)	O(2)-C(18)-C(17)	122.7(4)
C(15)-C(18)-C(17)	114.6(3)	C(16)-C(19)-C(22)	121.6(4)
C(16)-C(19)-H(19)	118.0(22)	C(22)-C(19)-H(19)	120.4(22)
C(17)-C(20)-C(21)	119.5(4)	C(17)-C(20)-C(23)	121.6(3)
C(21)-C(20)-C(23)	118.8(4)	C(20)-C(21)-C(25)	120.0(5)
C(20)-C(21)-H(21)	115.2(22)	C(25)-C(21)-H(21)	124.8(22)
C(4)-C(22)-C(19)	118.7(4)	C(4)-C(22)-H(22)	120.1(22)
C(19)-C(22)-H(22)	121.1(22)	O(3)-C(23)-C(9)	123.9(4)
O(3)-C(23)-C(20)	121.1(4)	C(9)-C(23)-C(20)	114.9(4)
C(15)-C(24)-H(24A)	111.0(22)	C(15)-C(24)-H(24B)	111.5(24)
C(15)-C(24)-H(24C)	108.4(22)	H(24A)-C(24)-H(24B)	109.5(32)
H(24A)-C(24)-H(24C)	107.0(32)	H(24B)-C(24)-H(24C)	109.4(33)
C(21)-C(25)-C(28)	120.5(4)	C(21)-C(25)-H(25)	119.7(25)
C(28)-C(25)-H(25)	119.8(25)	C(17)-C(26)-C(28)	119.7(5)
C(17)-C(26)-H(26)	118.5(24)	C(28)-C(26)-H(26)	121.6(24)
O(1)-C(27)-H(27A)	114.4(24)	O(1)-C(27)-H(27B)	111.5(26)
O(1)-C(27)-H(27C)	104.1(25)	H(27A)-C(27)-H(27B)	102.7(36)
H(27A)-C(27)-H(27C)	104.4(35)	H(27B)-C(27)-H(27C)	119.9(35)
C(25)-C(28)-C(26)	120.4(5)	C(25)-C(28)-H(28)	120.3(25)
C(26)-C(28)-H(28)	119.2(25)		


C(28)
C(25)
C(21)
C(26)
C(17)
C(20)
C(18)
C(23)
O(2)
C(24)
O(3)
C(15)
C(9)
C(4)
C(8)
C(22)
C(5)
C(10)
C(6)
C(14)
C(19)
C(11)
C(7)
C(12)
O(1)
C(16)
C(13)
C(27)

An attempt to cause photoreaction of diphenyl substituted **1d** with donor anisole or 1, 3, 5-trimethoxybenzene was failed even in the presence of excess $Mg(ClO_4)_2$, although the intermolecular PET is expected to be feasible from the value of ΔG for anisole (-112 kJ mol^{-1} according to the Rehm-Weller equation[11]) as well as the fluorescence quenching experiment with anisole. Fluorescence of **1d** was quenched by anisole. Stern-Volmer plots of the fluorescence quenching were linear for anisole concentration, indicating the ET to singlet excited state of **1d**.

3-3 Conclusion

The present results sugget that the intramolecular PET coupled with the assistance of metal ion is essential for photoconversion of the intrinsically less labile methyl-substituted homoquinones. Namely, the two radical centers must be developed across the cyclopropane moiety so as to achieve its ring-cleavage through the cooperative β-fission.

3-4 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 Me_4Si(δ 0.00) as an internal standard. IR, ultraviolet and fluorescense 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 300W high pressure Hg lamp, and the short cut filter used were an Eikohsha glass filter FT-3 (>330nm). All crystallographic measurements were made using a MAC science MXC3 diffractometer. Empirical absorption corrections (ψ-scan) were applied. The structure was solved by direct methods (SIR) and refined by full-matrix least squares analysis using 4273 unique reflections to final R factor= 0.0471, Rw= 0.0434. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

Anisyl-linked homonaphthoquinones, **1j**, ***endo*-1k** and ***exo*-1k** were synthesized from the reaction of dianisyldiazomethane or anisylphenyldiazomethane with 2-methylnaphthoquinone in benzene for 24h. *Exo* and *endo* isomer were separated by column chromatography on silica gel by using hexane-benzene as an eluent. The high melting point isomer was ascertained as *endo* isomer on the basis of the ^{1}nmr analysis.

2-Methyl-3-dianisilmethylene-2,3-dihydro-1,4-naphthoquinone (1j).

m.p. 90-91°C. Colorless prisms(from benzene);IR(KBr) 1670, 1510, 1331,1294, 1029 cm^{-1}. ^{1}H NMR($CDCl_3$) δ 7.81-7.84 (m,2H), 7.77-7.74 (m,2H) 7.43-7.41 (m,2H), 7.00 (d, J=8.56, 2H), 6.82 (d, J=8.58, 2H), 6.39 (d, J=8.19, 2H), 3.74 (s,3H), 3.52 (s,3H), 3.22 (s,1H), 1.38 (s,3H). Anal. Calcd for $C_{26}H_{22}O_4$ C; 78.37, H; 5.56. Found: C; 80.65, H; 6.06.

Photoreaction of Homonaphthoquinone (1k,l) in the Presence of $Mg(ClO_4)_2$.

Irradiation of **1j** (50mg) with 5 equiv. of $Mg(ClO_4)_2$ (140 mg) in acetonitrile (20 ml) was carried out under an atmosphere of nitrogen with a high pressure mercury lamp through a filter (>330nm) for 2h.. After irradiation, the solvent was evaporated and the reaction mixture was submitted for ^1H NMR analysis to determine the yield of **15a**. The product **15a** was extracted with benzene(10 ml x 2) from the aqueous solution of the reaction mixture, and the organic layer was dried over $MgSO_4$ and evaporated. The residue was chromatographed on silica gel to give **15a** (41mg, 82%) with a mixture of hexane and benzene as an eluent.

5,5-di(p-Methoxyphenyl)-11a-methyl-11aH-benzo[b]fluorene-6,11-dione (15a).

M.p. 187-189°C. Yellow prisms. IR(KBr) 1696, 1507, 1344,1248, 1034 cm^{-1}. ^1H NMR(CDCl3) δ 8.11-8.24 (m,2H),7.94 (d,J=7.59,1H) 7.68-7.75 (m,4H) 7.56 (d,J=8.25, 1H), 7.49 (d, J=8.25, 1H),7.42 (d, J=7.26,1H), 7.03 (d, J=8.25, 2H) , 3.89 (s,3H), 1.78 (s,3H). MS; Calcd for $C_{25}H_{18}O_3$: 366.1256. Found (HRMS): 366.1248.

5-(p-Methoxyphenyl)-11a-methyl-11aH-benzo[b]fluorene-6,11-dione (15b).

M.p. 112-113°C. Yellow prisms. IR(KBr) 1670, 1510, 1331,1294, 1029 cm^{-1}. ^1H NMR($CDCl_3$) δ 8.09-8.23 (m,2H), 7.68-7.74 (m,4H) 7.48 (d, J=2.64, 1H), 7.39 (d, J=8.58, 1H), 7.02 (d, J=8.58, 2H), 6.95 (dd, J_1=2.64, J_2=8.58, 1H), 3.96 (s,3H), 3.89 (s,3H), 1.77 (s,3H). MS(EI)=396 (M+). Anal. Calcd for $C_{26}H_{20}O_4$: C; 78.76, H; 5.23. Found: C; 78.75, H; 5.09.

3-5 References

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