

## Photoinduced Reductive Cleavage of Diarylcyclopropanes fused with Bromonaphthoquinone in the Presence of Amines

Hiroshi Moriwaki, Takumi Oshima and Toshikazu Nagai\*

*Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka, 560, Japan*

Irradiation of diarylcyclopropanes **1** fused with 2-bromonaphthoquinone in the presence of amines results in the dimerization of the intermediary allyl radicals **4**, formed by the reductive cleavage of the cyclopropane ring.

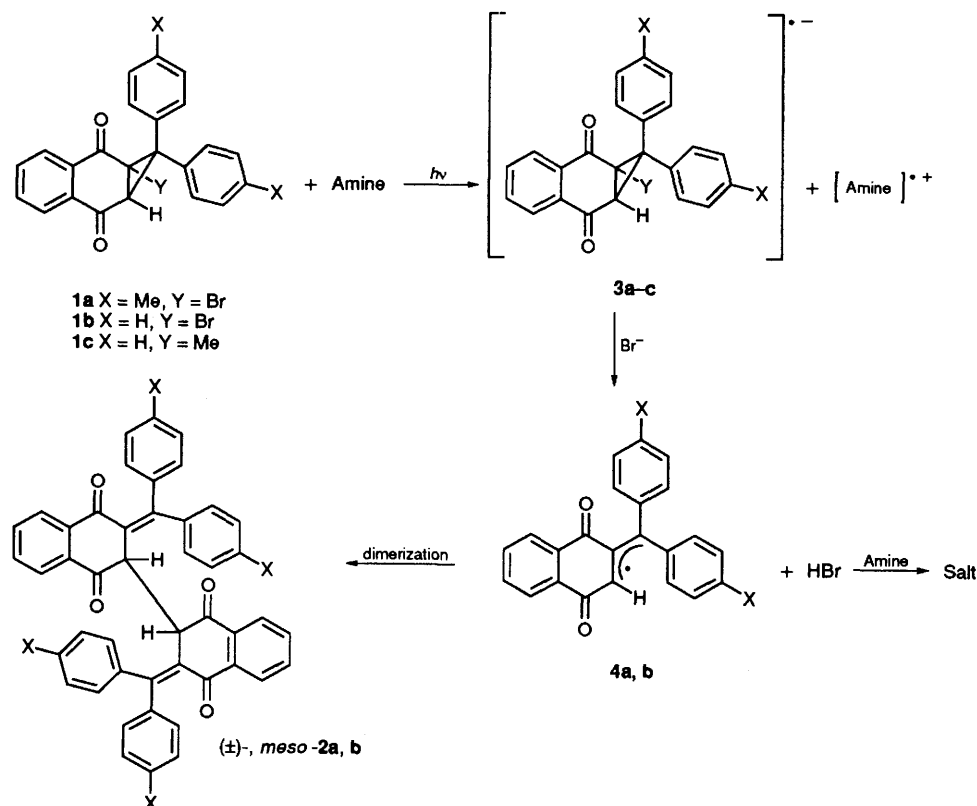
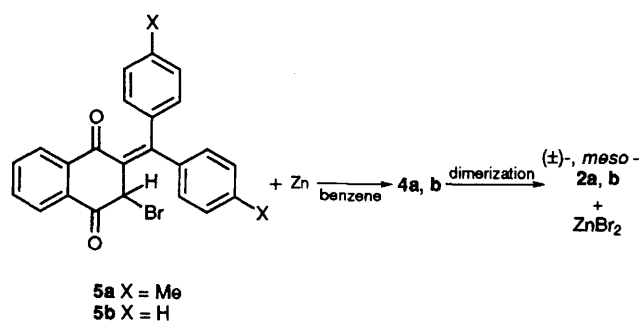
Photoinduced electron-transfer (PET) reactions have received much attention and intensive studies have been made of a variety of donor-acceptor systems to explore the mechanistic details.<sup>1</sup> During the past decade, PET reactions of cyclopropanes bearing several phenyl groups acting as a chromophore have been studied to understand the physico-chemical properties due to the strain of the small ring and to shed light on the potential utility of them as synthetic intermediates,<sup>2</sup> where phenylcyclopropanes behave as the electron donor. On the other hand, very few examples are known about photoreactions of diphenylcyclopropanes with electron-withdrawing groups like CN and Br in the presence of TEA.<sup>3</sup>

This paper reports that the photoreactions of diarylcyclopropanes **1a,b** fused with bromonaphthoquinone in the presence of various amines give the dimeric isomers ( $\pm$ )-**2a,b** and *meso*-**2a,b**,<sup>†</sup> through the reductive ring opening followed by dimerization of the resulting allyl radicals.

Irradiation of cyclopropanes **1a,b** (2.5 mmol dm<sup>-3</sup>) and 5 equiv. excess of TEA, DEA or DMA in various solvents under an atmosphere of nitrogen with a high pressure mercury lamp through a filter ( $\geq 330$  nm) for 2 h afforded the dimeric products ( $\pm$ )-**2a,b** and *meso*-**2a,b** together with the hydrogen bromide salt of the respective amines.

The general preparative procedure is represented for the case of **1b** (50.0 mg) and TEA (62.8 mg) in acetonitrile. After irradiation, the solvent and excess amine were evaporated and the reaction mixture was submitted for <sup>1</sup>H NMR analysis<sup>‡</sup> to

determine the conversion of **1b** and the yield of products by using an internal standard. The reaction mixture was washed with benzene (5 ml  $\times$  3) to remove 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 unconsumed **1b** (11 mg, 22%) and ( $\pm$ )-**2b** (7 mg, 22%) with a mixture of hexane and benzene as an eluent, and *meso*-**2b** (6 mg, 19%) and amine salt of hydrogen bromide (1 mg, 6%) with a mixture of benzene and diethyl ether, and finally a considerable amount of intractable resinous material (10 mg) with methanol. The dimeric isomer ( $\pm$ ) and *meso*-**2b** were essentially photostable on irradiation in the presence of amine. In harmony with this fact, the yield of the dimeric products was not improved at low conversion (27.3%, entry 3, Table 1).



**Table 1** Photoreaction of diarylcyclopropanes **1** with several amines

Entry	Cyclopropane	Donor	Solvent	Irrad. time/min	$\Delta G^a$ /kJ mol <sup>-1</sup>	Conv. (%)	Yield (%) <sup>b,c</sup>			Salt
							(±)-2	meso-2	(±):meso	
1	<b>1a</b>	TEA	MeCN	120		56.7	11.7	10.5	(1.1)	55.7
2	<b>1b</b>	TEA	MeCN	120	-183	72.6	26.0	23.2	(1.1)	78.2
3	<b>1b</b>	TEA	MeCN	40		27.3	25.5	21.5	(1.2)	86.3
4	<b>1b</b>	TEA	EtCN	120		51.1	29.8	22.9	(1.3)	68.3
5	<b>1b</b>	TEA	CH <sub>2</sub> Cl <sub>2</sub>	120		69.2	14.7	12.9	(1.1)	85.3
6	<b>1b</b>	TEA	MeCO <sub>2</sub> Et	120		69.5	12.5	10.0	(1.3)	69.5
7	<b>1b</b>	TEA	THF	120		64.8	10.4	7.76	(1.4)	63.2
8	<b>1b</b>	TEA	C <sub>6</sub> H <sub>6</sub>	120		62.3	16.7	12.3	(1.3)	72.6
9	<b>1b</b>	DEA	MeCN	120	-181	57.8	17.4	14.8	(1.4)	75.8
10	<b>1b</b>	DMA	MeCN	120	-179	62.1	21.7	18.8	(1.2)	61.4 <sup>d</sup>
11	<b>1b</b>	—	MeCN	120		0	0	0	—	0
12	<b>1b</b>	TEA	MeCN	0		0	0	0	—	0
13	<b>1c</b>	TEA	MeCN	120	-212	0	0	0	—	0

<sup>a</sup> Calculated according to Weller equation<sup>4</sup>:  $E_{0,0}$  of **1b** and **1c** was measured to be 3.70 and 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  $E_p = -1.22$  V in MeCN. Oxidation potentials of TEA, DEA and DMA vs. SCE are 0.76, 0.78 and 0.81 V, respectively.<sup>1</sup> <sup>b</sup> Owing to the NMR peak areas of methine protons of (±)-2, meso-2 and remaining **1** and of methylene protons of salts with respect to the methylene peak area of 4-(chloromethyl)-biphenyl was used as an internal standard. <sup>c</sup> Calculated on the consumed diarylcyclopropane **1**. <sup>d</sup> Isolated yield.

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

	Reaction time/h	Conv. (%)	Yield (%) <sup>a</sup>		
			(±)-2	meso-2	(±):meso
<b>5a</b>	1	100	32.6	13.1	(2.5)
<b>5b</b>	1	100	49.5	18.9	(2.6)

<sup>a</sup> Determined by NMR spectroscopy as in Table 1.

The results are summarized in Table 1. The fluorescences of **1** were quenched by TEA. Stern–Volmer plots of the fluorescence quenching were linear for amine concentration, indicating the electron transfer to the singlet excited state of **1**. The value of  $k_q$  obtained from the slope of Stern–Volmer plots of **1b** was  $2.90 \times 10^9$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>.<sup>§</sup> No new emission attributable to exciplex fluorescence was observed in the quenching experiments.

The values of (±):meso ratio were not markedly affected by varying the substituent (X) of **1** (entries 1 and 2), solvents (entries 2 and 4–8), as well as donor amines (entries 2, 9 and 10). Free energy changes ( $\Delta G$ ) calculated according to the Weller equation<sup>4</sup> for the system of **1b** and various amines are all negative. This means electron transfer from amines to excited **1b** should be spontaneous. No charge-transfer absorption appeared in the mixture of **1** and 5 equiv. excess of amines in acetonitrile solution, indicating the absence of appreciable interaction in the ground state. These reactions did not occur in the absence of amine or in the dark (entries 11 and 12). Furthermore, the replacement of the labile bromo substituent of **1b** by the methyl group endowed it with photopersistency as noted in **1c** (entry 13), though the initial photoelectron transfer is expected to be feasible from the value of  $\Delta G$  as well as the fluorescence quenching experiment with TEA. 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** accompanied by a single electron transfer from the amine to the excited **1**. The radical anion **3a,b** undergoes ring opening with loss of bromide to generate allyl radical **4a,b**. Here, the possible radical anion of **1c** (Y = Me) will give back the electron to the amine radical cation. The radical **4a,b** will collapse to the dimer **2a,b**. The extruded bromide abstracts a proton from the counter radical cation of the amine to form the salt with another molecule of amine.

In order to confirm the participation of an allyl radical in the present dimerization process, we attempted the redoxical debromination of allyl bromides, **5a,b** with zinc powder. This

simple system also gave (±)- and meso-**2a,b** most probably via the allyl radical **4a,b**, supporting strongly the proposed photodimerization mechanism (Table 2, Scheme 2).

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## Footnotes

† Spectroscopic data for (±)-**2b**: mp 288–290 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): 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); *m/z* 646 (M<sup>+</sup>); satisfactory elemental analysis were obtained. For meso-**2b**: mp 278–279 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 4.38 (2H, s), 6.73–6.77 (4H, m), 7.04–7.08 (4H, m), 7.13–7.17 (6H, m), 7.21–7.26 (6H, m), 7.62–7.66 (4H, m), 7.80–7.86 (4H, m); *m/z* 646 (M<sup>+</sup>); satisfactory elemental analyses were obtained. The other dimeric products, (±)-meso-**2a**, also provided satisfactory analytical and spectroscopic data. The (±)- and meso isomers of **2** were separated by column chromatography on silica gel. Stereochemistry of dimers, **2** [meso and (±)], was determined by using a NMR chiral shift reagent, tris[3-heptafluoropropylhydroxymethylene-(+)-camphorato]europium(III) derivative. The high field methine singlet (δ 4.34 for **2a** and 4.30 for **2b** in CDCl<sub>3</sub>) 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 (δ 4.41 for **2a** and 4.38 for **2b**) of another isomer was not split. The former high field isomer was assigned as the (±)-form, and the latter one as the meso-form.

‡ Also analysed by reversed-phase HPLC, which showed the presence of at least seven by-products eluted prior to the unconsumed **1b** and meso- and (±)-**2b**. Some of these products may be owing to the side pathway via the allyl radical (**4b**). However, we could not isolate them by careful chromatography on silica gel.

§ Fluorescence lifetime of **1b** was measured to be 5.36 ns.

¶ Compounds **5a,b** were provided by thermolysis of **1a,b** at 100 °C in toluene. Details will be described elsewhere.

|| Rather higher (±):meso ratios compared to the photoreaction may be ascribed to some interaction between the radicals **4a,b** and Zn.

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