

Photoamination of 1,2-Diarylcyclopropanes Using 2,2'-Dialkoxy-1,1'-binaphthalene as Redox-Photosensitizer

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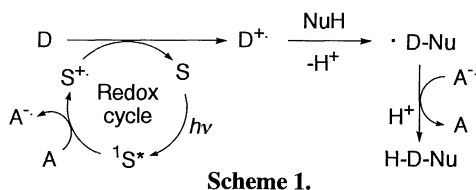
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1-Amino-1,3-diarylpropanes were prepared by the photoamination of 1,2-diarylcyclopropanes with NH₃, using 2,2'-dialkoxy-1,1'-binaphthalene and *m*-dicyanobenzene as sensitizers and electron acceptor.

Redox-photosensitization is one of the most powerful methods to achieve efficient reactions via photoinduced electron transfers.¹ The redox-photosensitization by a pair of arenes (e.g. phenanthrene) and dicyanobenzene acting as a sensitizer (S) and an electron acceptor (A) has been successfully applied to photoinduced nucleophilic addition of alcohols to a variety of electron-donating substrates (D).^{1b,2} The redox-photosensitization is especially effective in such cases where D has only weak or no absorption at longer wavelength.² As shown in Scheme 1, the photosensitized nucleophilic addition proceeds via the photoinduced electron transfer from S to A, followed by a hole transfer from the cation radical of S to D, and the subsequent addition of nucleophiles (NuH) to the cation radical of D.

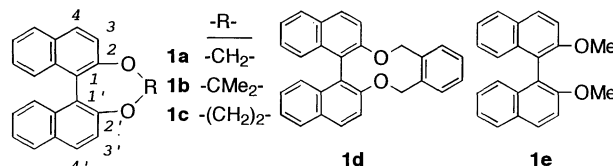


Scheme 1.

On the other hand, our investigation on the photoinduced nucleophilic addition of RNH₂ (photoamination) has elucidated that RNH₂ readily reacts with the cation radicals of a variety of arenes, thus showing that the redox-photosensitization using arenes as S can hardly be applied to the photoamination process.³ Moreover, the usual electron-transfer photosensitization by A (e.g. 9,10-dicyanoanthracene) is ineffective for the photoamination due to the quenching of the excited state of A by RNH₂. Therefore, the photoamination has been restricted to the substrates which have absorption at longer wavelength.

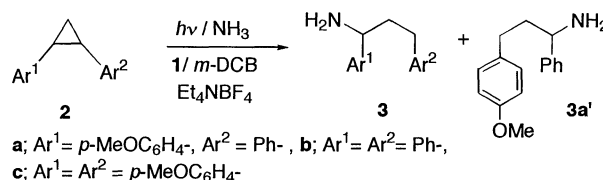
Recently we have found that the cation radicals of 1-substituted 2-alkoxynaphthalenes are inert to NH₃ in the photoamination of alkenylnaphthalenes.⁴ Therefore, we are now interested in redox-photosensitized amination using 2,2'-dialkoxy-1,1'-binaphthalene derivatives (**1**) as S (Scheme 2). (*E*)-1-(*p*-Methoxyphenyl)-2-phenylcyclopropane (**2a**), a mixture of (*Z*)- and (*E*)-1,2-diphenylcyclopropane (**2b**), and (*E*)-1,2-di(*p*-methoxyphenyl)cyclopropane (**2c**) were selected as D.⁵ *m*-Dicyanobenzene (*m*-DCB) was used as A, because of the relatively clean reaction compared to that of *p*-DCB.⁶

Irradiation of an ammonia-saturated MeCN-H₂O (9:1 v/v; 70 cm³) solution containing **1a** (1 mmol), **2a** (3 mmol), *m*-DCB (3.5 mmol), and Et₄NBF₄ (70 mmol) by a high-pressure Hg



Scheme 2. Redox-photosensitizer (S).

lamp through a Pyrex filter ($\lambda > 280$ nm) produced 1-amino-1-(*p*-methoxyphenyl)-3-phenylpropane (**3a**) and 1-amino-3-(*p*-methoxyphenyl)-1-phenylpropane (**3a'**) in a ratio of 1:0.3. The results were shown in Scheme 3 and Table 1. Irradiation in the absence of *m*-DCB gave **3a** in poor yield (entry 2). Without Et₄NBF₄,⁷ the photoamination slowed down (entry 3). Direct irradiation of *m*-DCB in the absence of **1a** gave **3a** in low conversion (entry 4). The photosensitized amination using **1d** and **1e** proceeded in low yield (entries 7 and 8). The photosensitization by **1a** was applied to the amination of **2b** and **2c**, which gave **3b** and **3c** as sole products. All cases of **1** were recovered in >75%, except for the case of **1b** which was



Scheme 3.

Table 1. Amination of **2a-c** with NH₃ photosensitized by **1a-e**^a

Entry	1	2 (E ^{ox} /V) ^b	3 ^c Yield/%	Conv. / %	Recovery of 1 / %	
1	1a	2a (+0.93)	3a	79	100	82
2 ^d	1a	2a	3a	6	8	76
3 ^e	1a	2a	3a	32	35	87
4 ^f	none	2a	3a	41	52	-
5	1b	2a	3a	58	100	37
6	1c	2a	3a	89	100	79
7	1d	2a	3a	56	100	75
8	1e	2a	3a	47	100	92
9	1a	2b (+1.06)	3b	40	53	87
10	1a	2c (+0.92)	3c	90	100	75

^a Irradiation for 20 h. After the photoreaction, *m*-DCB was recovered in >80% yield. ^b Half peak of oxidation potentials in MeCN vs. Ag/AgNO₃. ^c The isomer ratio of **3a** to **3a'** was 1:0.3. ^d In the absence of *m*-DCB. ^e In the absence of Et₄NBF₄. ^f Direct irradiation of *m*-DCB with **2a** in the absence of **1**.

Table 2. Characterization of **1** and charge distribution on the selected carbon in **1**⁺.

1	E ^{OX} ^a	E ⁰⁻⁰ ^b	τ_f ^c	ΔG ^d	k_q ^e	Charge Distribution ^f								$\theta/^\circ$ ^g
	V	kJ mol ⁻¹	ns	kJ mol ⁻¹	10 ¹⁰ M ⁻¹ s ⁻¹	C4	C3	C2	C1	C1'	C2'	C3'	C4'	
1a	+1.18	303	2	8	1.3	0.03	-0.12	0.13	0.05	0.05	0.13	-0.12	0.03	44
1b	+1.17	321	9	-11	0.7	0.03	-0.12	0.15	0.05	0.05	0.15	-0.12	0.03	44
1c	+1.14	334	3	-26	1.8	0.03	-0.13	0.13	0.06	0.06	0.13	-0.13	0.03	54
1d	+1.05	326	4	-27	2.0	0.12	-0.25	0.29	0.09	-0.08	0.11	-0.14	-0.02	61
1e	+1.01	327	5	-31	2.8	0.12	-0.26	0.26	0.12	-0.13	0.12	-0.16	-0.01	71

^a Half wave of oxidation potentials in MeCN vs. Ag/AgNO₃. ^b Excitation energy for the excited singlet of **1** determined by the fluorescence spectra. ^c Lifetimes of the fluorescence in MeCN under deaerated conditions. ^d Free energy change for the electron transfer from the excited singlet state of **1** to *m*-DCB ($E^{\text{red}} = -2.11$ V) calculated by Rehm-Weller equation (ref. 8). ^e Rate constant for the fluorescence quenching of **1** by *m*-DCB in MeCN. ^f Carbon numbering is shown in Scheme 2. ^g Dihedral angle of C2-C1-C1'-C2'.

hydrolyzed to 2,2'-binaphthol during the photoreaction.

Under the reaction conditions, almost all incident light was absorbed by **1**, since molar absorptivity at 300 nm for **1a-e** and **2a-c** was 1.7-0.5 $\times 10^4$ and 2.1-8.8 $\times 10^2$ M⁻¹cm⁻¹, respectively. The fluorescences of **1a-e** were quenched by *m*-DCB at nearly diffusion-controlled rates, but were not at all quenched by **2** and NH₃. The free energy changes (ΔG) required for electron transfer from the excited singlet state of **1b-e** to *m*-DCB were calculated to be negative by the Rehm-Weller equation,⁸ using the half wave of oxidation potentials (E^{ox}) and excitation energy, while ΔG is slightly positive in the case of **1a**. However, the participation of the excited triplet state of **1** can not be completely ruled out, since the fluorescence lifetimes of **1** were short. Therefore, the present photoamination is initiated by an electron transfer from the excited singlet and triplet state of **1** to *m*-DCB which gives **1**⁺ and DCB⁻. It is well known that the reaction of the excited state of **2a** with RNH₂ can occur.⁹ In the present case however, the participation of the excited singlet and triplet states of **2a** generated by the energy transfer from the excited state of **1** can be ruled out, since the photoamination in the absence of *m*-DCB proved very inefficient.

Semiempirical calculation (PM3) of the ring-opened cation radical of **2a** showed that the positive charge developed over the benzylic carbon (C1) of the *p*-methoxyphenyl group but not at all over the benzylic carbon (C3) of the phenyl group.¹⁰ The formation of **3a'** can not be explained by the nucleophilic addition of NH₃ to the positive site of the ring-opened cation radical of **2a**. Therefore, the nucleophilic addition of NH₃ occurred at the ring-closed **2**⁺ to give a mixture of aminated radicals which were converted to **3a** and **3a'** by reduction by A⁻ and protonation. The isomer ratio of **3a** to **3a'** would depend on the relative stabilities of the aminated radicals. Dinnocenzo et al.¹¹ reported similar nucleophilic additions of MeOH to the ring-closed cation radicals of arylcyclopropanes.

The key pathway for the redox-photosensitization is the hole transfer from **1**⁺ to **2**. The efficiency of the hole transfer might depend on the difference between **1** and **2** in E^{ox} , along with the lifetime and structure of **1**⁺. For **1a-c**, whose E^{ox} were much higher than that of **2**, the efficient hole transfer from **1**⁺ to **2** would occur. The PM3 calculation showed that the distribution of the positive charge and the dihedral angles (θ) between two naphthyl rings in **1**⁺ were affected by the alkoxy substituents (Table 2). In the cation radicals of **1a-c**, where $\theta < 54^\circ$, the symmetric charge distribution on two naphthalene rings was

observed, thus showing that the positive charge delocalized over the two naphthalene rings. However, in the cation radicals of **1d-e**, where $\theta > 60^\circ$, and the positive charge distributed unsymmetrically, the positive charge should have delocalized on one naphthalene ring. The approach of **2** to the positive sites of the cation radicals of **1d-e** would be interfered by another naphthyl ring. Thus, the inefficient photosensitized amination by **1d-e** is attributable to the low E^{ox} of **1d-e** and the unfavorable structure of **1d-e**⁺ for the hole transfer.

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