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

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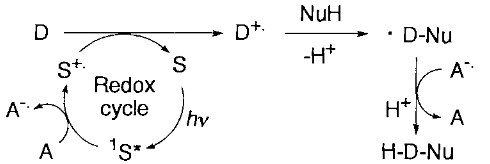
1-Amino-1,3-diarylpropanes were prepared by the photoamination of 1,2-diarylcyclopropanes with NH_3, using 2,2'-dialkoxy-1,1'-binaphthalene and *m*-dicyanobenzene as sensitizers and electron acceptor.

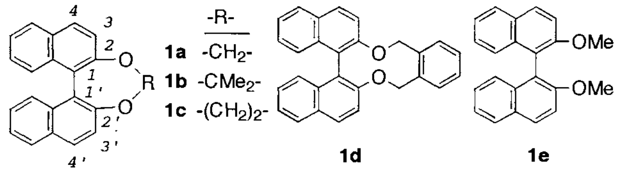
Redox-photosensitization is one of the most powerful methods to achieve efficient reactions via photoinduced electron transfers.[1] The redox-photosensitization by a pair of arenes (e.g. phenanthrene) and dicyanobenzene acting as a sensitizer (S) and an electron acceptor (A) has been successfully applied 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.

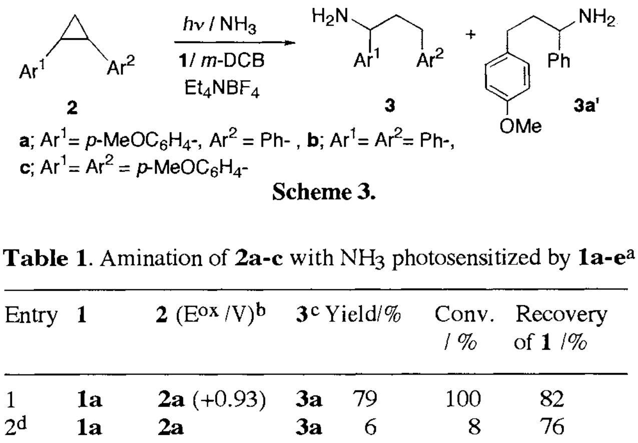
On the other hand, our investigation on the photoinduced nucleophilic addition of RNH_2 (photoamination) has elucidated that RNH_2 readily reacts with the cation radicals of a variety of arenes, thus showing that the redox-photosensitization using arenes as S can hardly be applied to the photoamination 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 RNH_2. 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 NH_3 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-diphenylcycpropropane (**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]



Scheme 2. Redox-photosensitizer (S).

Irradiation of an ammonia-saturated $MeCN-H_2O$ (9:1 v/v; 70 cm^3) solution containing **1a** (1 mmol), **2a** (3 mmol), *m*-DCB (3.5 mmol), and Et_4NBF_4 (70 mmol) by a high-pressure Hg lamp through a Pyrex filter (λ> 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 Et_4NBF_4,[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 NH_3 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/$AgNO_3$. [c] The isomer ratio of **3a** to **3a'** was 1:0.3. [d] In the absence of *m*-DCB. [e] In the absence of Et_4NBF_4. [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 $1^{+\cdot}$

1	E^{ox} a	$E^{0\text{-}0}$ b	τ_f c	ΔG d	k_q e	Charge Distribution f								θ/° 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/AgNO$_3$. [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^{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 1.7-0.5X10^4 and 2.1-8.8X10^2 M^{-1}cm^{-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 NH_3. 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 $1^{+\cdot}$ and $DCB^{-\cdot}$. It is well known that the reaction of the excited state of **2a** with RNH_2 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 NH_3 to the positive site of the ring-opened cation radical of **2a**. Therefore, the nucleophilic addition of NH_3 occurred at the ring-closed $2^{+\cdot}$ to give a mixture of aminated radicals which were converted to **3a** and **3a'** by reduction by $A^{-\cdot}$ 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 $1^{+\cdot}$ 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 $1^{+\cdot}$. For **1a-c**, whose E^{ox} were much higher than that of **2**, the efficient hole transfer from $1^{+\cdot}$ 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 $1^{+\cdot}$ were affected by the alkoxy substituents (Table 2). In the cation radicals of **1a-c**, where θ<54°, 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 θ>60°, 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 $\mathbf{1d\text{-}e}^{+\cdot}$ for the hole transfer.

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