Photoreduction of 1,2-Diarylcyclopropanes by Hydroxide Ion

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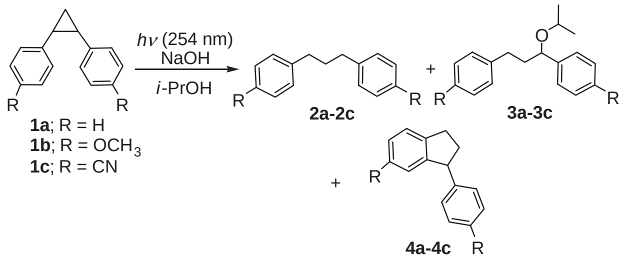
The photoreduction of 1,2-diarylcyclopropanes **1** by NaOH yielded the corresponding 1,3-diarylpropanes **2** in *i*-PrOH. The efficiency of the photoreduction was dependent on the electron deficiency of **1** and the excitation wavelength, solvent, and additive. This is a rare example of a cyclopropane serving as an electron acceptor to afford a reduction product.

The photochemistry of cyclopropanes has been actively investigated owing to their characteristic reactivity.[1] In particular, cyclopropanes can be utilized as good electron donors in a photoinduced electron-transfer (PET) reaction because of their low oxidation potentials. While PET reactions of cyclopropanes with a variety of electron acceptors have been developed,[2] the only reported example of the PET of cyclopropanes with an electron donor is with tertiary amines.[3] In the latter case, the photoreaction of electron-deficient cyclopropanes such as alkoxycarbonylcyclopropane derivatives yields an amine adduct as the major product along with a reduction product through the formation of the radical anion.

We have recently reported that the photochemical Birch-type reduction of arenes and the photodehalogenation of haloarenes using a hydroxide ion as an electron source.[4] The photoreaction by the hydroxide ion could offer many advantages from economical, environmental, and safety standpoints. In this letter, we report on the photoreduction of 1,2-diarylcyclopropanes by the hydroxide ion in *i*-PrOH. This is a rare example of a cyclopropane serving as an electron acceptor to afford a reduction product. In addition, this photoreaction techinique can provide an environmentally friendly method for the reduction of arylcyclopropanes, compared to the conventional reduction techinique using H_2 and Pd/C.[5]

Initially, the photoreduction of 1,2-diarylcyclopropanes **1a**–**1c** with NaOH by 254-nm light in *i*-PrOH was examined. Irradiation was carried out in quartz vessels with a 120-W low-pressure mercury lamp under an argon atmosphere at room temperature. The excitation of a *i*-PrOH solution of 1,2-diphenylcyclopropane (**1a**) (2 mM) and NaOH (250 mM) for 2 h afforded reduction product **2a** and alcohol adduct **3a** in 26% and 13% isolated yields, respectively (Entry 1 in Table 1);[6] however, in the absence of NaOH, **2a** was not obtained (Entry 4). Lower concentrations of NaOH caused a decrease in the yield of **2a** (Entries 2 and 3). Thus, the yield of the reduction product **2a** was highly dependent on the concentration of NaOH. In the photoreaction, the OH adduct was not obtained. When 1,2-di(4-methoxyphenyl)cyclopropane (**1b**) having an electron-donating group was subjected to photoreaction, the yield of reduction product **2b** was very low (Entry 5). In contrast, the photoreaction of 1,2-di(4-cyanophenyl)cyclopropane (**1c**) having an electron-withdrawing group yielded reduction product **2c** as the major product (Entry 6). Even with low concentrations NaOH (100 or 2 mM), similar yields of **2c** were obtained (Entries 7 and 8). Thus, the photoreduction of electron-deficient 1,2-diarylcyclopropane **1c** by NaOH smoothly proceeded in *i*-PrOH to yield the corresponding 1,3-diarylpropane **2c**.

Table 1. Photoreduction of **1a**–**1c** by NaOH in *i*-PrOH[a]



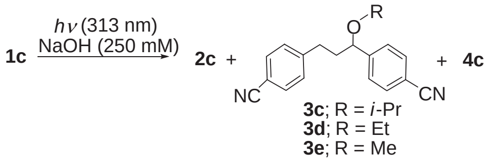
Entry	1	NaOH/mM	Product yields/%[b,c]			Recovery of 1/%[b]
			2	3	4	
1	**1a**	250	26	13	0	15
2	**1a**	100	13	8	4	46
3	**1a**	2	0	5	4	55
4	**1a**	0	0	4	4	57
5	**1b**	250	3	18	0	68
6	**1c**	250	38	0	9	trace
7	**1c**	100	40	trace	5	9
8	**1c**	2	33	14	12	15

[a] The photoreaction was carried out with 0.8 mmol (2 mM) of **1** and NaOH in quartz vessels using a 120-W low-pressure mercury lamp under an argon atmosphere for 2 h. [b] Isolated yield. [c] Characterization data of these products are shown is Supporting Information.[11]

Next, the effects of the excitation wavelength, solvent, and additive on the photoreduction of **1c** were examined. Prolonged irradiation of the *i*-PrOH solution containing **1c** and NaOH by 254-nm light decreased the yield of **2c**, since the secondary photoreduction of the benzene group of **2c** by NaOH could take place, as reported earlier.[4] In fact, the photoreaction of **2c** (2 mM) with NaOH (250 mM) in *i*-PrOH for 2 h recovered **2c** in only 20% yield. In order to prevent the secondary photoreduction of the product **2c**, the excitation was carried out for 3 h at a longer wavelength (313 nm) using a 400-W high-pressure mercury lamp with Pyrex vessels. Under such conditions, the yield of the reduction product **2c** was slightly improved (Entry 1 in Table 2). Instead of *i*-PrOH, the use of EtOH as the solvent decreased the yield of **2c** (Entry 2), while the use of MeOH did not afford the reduction product (Entry 3). When thiols such as cysteine and *t*-dodecanethiol were added, higher yields of **2c** were obtained (Entries 4 and 5), and Entry 5 shows the highest yield of **2c**.

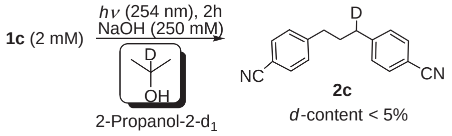
From a mechanistic viewpoint, we examined the deuterium incorporation experiment of **1c** using 2-propanol-2d_1 as a solvent (Scheme 1). The α-position to the aryl group of **2c** was not deuterated, indicating that *i*-PrOH did not serve as a hydrogen donor.

Table 2. Effects of solvent and additive on photoreduction of **1c** by irradiation at 313-nm light[a]

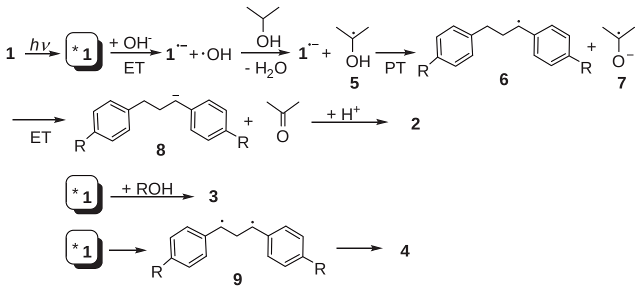


Entry	Solvent	Additive	Product yields/%[b,c]			Recovery of **1c**/%[b]
			2c	**3**	**4c**	
1	i-PrOH	—	44	7(**3c**)[d]	3	trace
2	EtOH	—	6	31(**3d**)[e]	6	17
3	MeOH	—	0	40(**3e**)[f]	5	22
4	i-PrOH	Cysteine (4 mM)	48	7(**3c**)[d]	3	trace
5	i-PrOH	t-Dodecanethiol (4 mM)	54	trace(**3c**)[d]	0	0

[a] The photoreaction was carried out with 0.8 mmol (2 mM) of **1c** in Pyrex vessels using a 400-W high-pressure mercury lamp under an argon atmosphere for 3 h. [b] Isolated yield. [c] Characterization data of these products are shown is Supporting Information.[11] [d] The alcohol adduct was **3c**. [e] The alcohol adduct was **3d**. [f] The alcohol adduct was **3e**.



Scheme 1. Deuterium incorporation experiment of **1c** using 2-propanol-2d_1.



Scheme 2. Plausible mechanism of the photoreduction of **1**.

Scheme 2 shows a plausible mechanism for this photoreduction. The electron transfer (ET) from the hydroxide ion to excited **1** leads to the formation of the radical anion of **1** and OH radical. The generated OH radical could abstract a hydrogen atom from i-PrOH to form the radical **5**.[7] The proton transfer (PT) from the radical **5** to the radical anion of **1** generates the radical **6** and the radical anion **7**. Because the radical anion **7** is a much strong electron donor,[8] the secondary ET between the radical **6** and radical anion **7** can take place to afford the anion **8** and acetone. The protonation of the anion **8** yields the reduction product **2**. However, excited **1** is known to react with alcohols to yield the corresponding alcohol adducts **3** or rearrange to yield **4** via the diradical **9**.[1,9] In the case of the photoreaction of **1b**, the low efficiency of the ET between the hydroxide ion and excited **1b** increases the yield of alcohol adduct **3b**. The use of EtOH or MeOH as the solvent causes an increase in the yield of alcohol adducts **3d** and **3e** because they have less steric hindrance than i-PrOH. In addition, the use of i-PrOH could efficiently generate the strong electron donor **7**. Thus, efficient photoreduction of cyclopropanes by the hydroxide ion requires i-PrOH as a solvent. A slight enhancement in the yield of reduction product **2c** by the addition of thiols could be attributed to the acceleration of ET processes by thiolate ions.[10]

In conclusion, we found that the photoreduction of 1,2-diarylcyclopropanes **1** by NaOH occurred in i-PrOH. The presence of an electron-withdrawing group such as a cyano group on the aromatic ring increased the reactivity of the photoreduction. In addition, the efficiency of the photoreduction of cyclopropane was strongly influenced by the solvent used. An investigation of the detailed mechanism of the photoreduction by the hydroxide ion is currently in progress.

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6 After the photoreaction, the mixture was neutralized by 3 M HCl, and the solvent was evaporated. The residue was dissolved in ether, washed with water, dried over Na_2SO_4, and concentrated under a reduced pressure to yield the products. These products were isolated by column chromatography on silica gel (hexane/EtOAc).

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.

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