

## Hydroxide ion as electron source for photochemical Birch-type reduction and photodehalogenation

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### Abstract

The photochemical Birch-type reduction of arenes and the photodehalogenation of haloarenes by a hydroxide ion that acted as an electron source occurred in 2-PrOH. The efficiency of these photoreactions was dependent on the nature of the substrate, the concentration of NaOH, and the solvent used. These photoreactions provide an environmentally friendly method for the reduction of aromatic rings and dehalogenation.

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One of the current challenges with regard to organic synthesis is the development of new and cleaner processes that minimize the use of hazardous substances.<sup>1</sup> Although several environmentally friendly methods have been reported, one of the most efficient approaches is the use of photoreaction since light is a clean and powerful reagent to transform organic molecules.<sup>2–5</sup> In particular, a photochemical electron transfer reaction between electron donor–acceptor pairs can produce reactive species under mild conditions.<sup>6–8</sup>

The reduction of aromatic rings and the dehalogenation of haloarenes are the useful synthetic transformations of organic molecules. In addition, the dehalogenation of haloarenes is now considered to be more important for the decontamination of aromatic halides since haloarenes are deleterious environmental pollutants. Both the abovementioned reactions are usually carried out by using metals or organic metals. For example, Birch reduction using alkaline metals (Li and Na) as an electron source in liquid ammonia has been one of the most common methods for

the reduction of aromatic rings.<sup>9,10</sup> Moreover, in dehalogenation, tributyltin hydride is generally employed as a reagent in the presence of a catalytic amount of AIBN in toluene.<sup>11,12</sup> However, a less toxic and more stable reagent is desirable so that the reactions can be carried out in conventional solvents at room temperature. The photochemical electron transfer using a suitable electron source can provide alternative methods for these reactions. The photo-reduction of arenes<sup>13,14</sup> and the photodehalogenation of haloarenes<sup>15,16</sup> by using amines as an electron source have already been reported, although the yields of products were significantly low because of the formation of adducts with amines.

During the course of our study on an organic photochemical reaction using a photosensitive surfactant in water,<sup>17,18</sup> we found that the naphthyl group of the surfactant was photoreduced in aqueous NaOH solution to produce a Birch-type reduction product. This result indicates that the hydroxide ion could serve as an electron source for the photochemical reaction. Although the electron transfer (ET) between the hydroxide ion and the dinitroarenes<sup>19–24</sup> or the excited nitrobenzene<sup>25–28</sup> has already been reported, these investigations have been carried out mainly from a mechanistic viewpoint. In this Letter, we

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report the photoreduction of arenes and the photodehalogenation of haloarenes using NaOH in the presence of a hydrogen donor such as 2-PrOH. This photoreaction technique can serve as a safe, convenient, and environmentally friendly method for these reactions.

The photoreduction of arenes was carried out in Pyrex vessels (>300 nm) with a 500 W high-pressure mercury lamp under an argon atmosphere at room temperature.<sup>29</sup> The results are summarized in Table 1. The excitation of a 2-propanol solution of phenanthrene **1** (5 mM) and NaOH (200 mM) for 6 h exclusively afforded 9,10-dihydr-



phenanthrene **2** in 82% isolated yield (Table 1, entry 1). The efficiency of this photoreduction was highly dependent on both the nature of the substrate and the concentration of NaOH; further, the use of KOH or tetrabutylammonium hydroxide instead of NaOH resulted in a low yield of the reduction product.<sup>30</sup> The addition of cysteine (6 mM) to this solution accelerated the photoreduction and increased the yield of **2**, even with a low concentration of NaOH (entry 2). Instead of 2-PrOH, the use of EtOH or MeOH or aqueous CH<sub>3</sub>CN (H<sub>2</sub>O/CH<sub>3</sub>CN = 1:1) as a solvent in the presence of NaOH (40 mM) and cysteine

Table 1  
Photoreduction of arenes by NaOH

Entry	Arenes	Solvent	NaOH (mM)	Irradn time <sup>a</sup> (h)	Additive	Products (Yield <sup>b</sup> (%))
1	<b>1</b> (5 mM)	2-PrOH	200	6	—	<b>2</b> (82)
2	<b>1</b> (5 mM)	2-PrOH	40	8	Cysteine 6 mM	<b>2</b> (91)
3	<b>3</b> (5 mM)	2-PrOH	40	4	—	<b>4</b> (70) + <b>2</b> (4)
4	<b>5</b> (5 mM)	2-PrOH	200	24	—	<b>6</b> (60)
5	<b>7</b> (2 mM)	2-PrOH	100	2	—	<b>8</b> (50) <sup>c</sup> + <b>9</b> (14) <sup>c</sup>
6	<b>10</b> (2 mM)	2-PrOH	200	2	—	<b>11</b> (32) + <b>12</b> (17)
7	<b>13</b> (2 mM)	2-PrOH	200	3	—	<b>14</b> (38) + <b>15</b> (25)
8	<b>16</b> (2 mM)	2-PrOH/H <sub>2</sub> O = 1:1	500	18	—	<b>17</b> (51) + <b>18</b> (3) + <b>19</b> (7)

(continued on next page)

Table 1 (continued)

Entry	Arenes	Solvent	NaOH (mM)	Irradn time <sup>a</sup> (h)	Additive	Products (Yield <sup>b</sup> (%))
9	<b>16</b> (2 mM)	2-PrOH	150	6	—	<b>17</b> (12) + <b>18</b> (34) + <b>19</b> (14)
10	<b>16</b> (2 mM)	H <sub>2</sub> O	500	3	Cysteine 40 mM	<b>17</b> (59) + <b>18</b> (2)
11	 <b>20</b> (2 mM)	2-PrOH/H <sub>2</sub> O = 1:1	500	0.7 <sup>d</sup>	—	 <b>21</b> (32)

<sup>a</sup> Irradiation was carried out with a 500 W high-pressure mercury lamp at room temperature.

<sup>b</sup> Isolated yield.

<sup>c</sup> Determined by GC analysis using authentic samples.

<sup>d</sup> Irradiation was carried out with a 120 W low-pressure mercury lamp at room temperature.

(6 mM) resulted in a low yield of **2** (33%, 21%, and 12%, respectively). Thus, the efficient photoreduction required a good hydrogen donor such as 2-PrOH. The photoreaction of 9-cyanophenanthrene **3** mainly yielded the reduction product **4**, but was accompanied by the decyanation product **2** (entry 3). Furthermore, the photoreaction of 9-methylphenanthrene **5** yielded the reduction product **6** (entry 4). When naphthalene derivatives were subjected to photoreaction, dihydro- and tetrahydronaphthalenes were formed (entries 5–10), and the regioselectivity of the photoreduction was dependent on both the substituent and the reaction conditions. The photoreduction of 1-methylnaphthalene **10** and 1-methoxynaphthalene **13** having an electron-donating group gave the corresponding 5,8-dihydro- and 5,6,7,8-tetrahydronaphthalenes (entries 6 and 7), while 1-carboxynaphthalene **16** in aqueous 2-PrOH solution yielded 1,4-dihydro-, 3,4-dihydro-, and 1,2,3,4-tetrahydronaphthalenes **17–19** (entry 8). It should be noted that the reduction product distribution changed with the solvent used. The use of 2-PrOH as a solvent mainly produced the corresponding 3,4-dihydronaphthalene **18** (entry 9), and the addition of cysteine (40 mM) in water yielded the corresponding 1,4-dihydronaphthalene **17** as the major product (entry 10).<sup>31</sup> The tetrahydronaphthalenes could be produced by the secondary photoreduction of the corresponding 1,2-dihydro-, 3,4-dihydro-, 5,6-dihydro-, and 7,8-dihydronaphthalenes with the hydroxide ion. In fact, the photoreaction of isolated 3,4-dihydronaphthalene **18** (5 mM) with NaOH (150 mM) in 2-PrOH for 6 h yielded tetrahydronaphthalene **19** in 45% isolated yield. In addition, benzoic acid **20** was also reduced by irradiation in aqueous 2-PrOH solution using a 120 W low-pressure lamp with quartz vessels to yield 1-carboxy-1,4-dihydrobenzene **21** in 32% isolated yield (entry 11). Thus, arenes such as phenanthrene, naphthalene, and benzene derivatives can be photoreduced by the hydroxide ion in the presence of a hydrogen donor such as 2-PrOH.

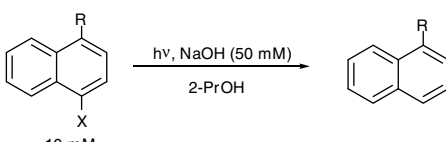
Next, the photochemical dehalogenation of haloarenes by the hydroxide ion was examined. A low power light source (a 100 W high-pressure mercury lamp) was adequate for this photoreaction under the same conditions. The 2-PrOH solution containing haloarenes **22a–f**, **24**, and **25**

(10 mM) and NaOH (50 mM) was irradiated to give the corresponding dehalogenated product (Table 2),<sup>29</sup> and further irradiation yielded the Birch reduction products. The presence of electron withdrawing group such as the cyano group on the aromatic ring increased the reactivity of the photoreaction (entry 5). In the case of 1,4-dibromonaphthalene **22e**, successive dehalogenation proceeded to provide a good yield of naphthalene **7** (entry 6). While the addition of cysteine was not effective in this photoreaction, the addition of *t*-dodecanethiol increased the yield of dehalogenated products (entries 3 and 9). Instead of 2-PrOH, the use of MeOH or EtOH or aqueous CH<sub>3</sub>CN as a solvent decreased the yield of dehalogenated products, irrespective of the presence and absence of *t*-dodecanethiol. Thus, the photodehalogenation also required a good hydrogen donor such as 2-PrOH.

The fluorescence of **1** was not quenched by the hydroxide ion, and the formation of the reduction product **2** was quenched by molecular dioxygen. In addition, the higher efficiency of dehalogenation than that of Birch-type reduction could be attributed to the heavy atom effect. From these results, we propose that the ET from the hydroxide ion to the excited triplet state of arenes or haloarenes is effected, leading to the formation of the radical anion. In the case of the photoreaction of 1-bromonaphthalene **22a**, the anion radical of **22a** generates through the ET between the hydroxide ion and the excited triplet state of **22a** (Scheme 1). The dehalogenation of the anion radical of **22a** produces radical **27** to yield naphthalene **7** through the abstraction of a hydrogen atom from 2-PrOH. Further, **7** is photoreduced by the hydroxide ion to form the anion radical, and the successive protonation of 2-PrOH generates radical **28**. Similarly, the hydrogen abstraction of radical **28** gives the reduction product **8**. Although an enhancement in the efficiency of these photoreactions was observed by the addition of thiols, the reason for the enhancement is not clear at this stage.

In conclusion, we found that the hydroxide ion can be used as an electron source in the photoreduction of aromatic rings and photodehalogenation of haloarenes, although the mechanistic details of photoreaction by the hydroxide ion have not yet been elucidated. Compared to

Table 2  
Photodehalogenation of haloarenes by NaOH



**22a**; X = Br, R = H  
**22b**; X = Br, R = CH<sub>3</sub>  
**22c**; X = Br, R = OCH<sub>3</sub>  
**22d**; X = Br, R = CN  
**22e**; X = Br, R = Br  
**22f**; X = Cl, R = H

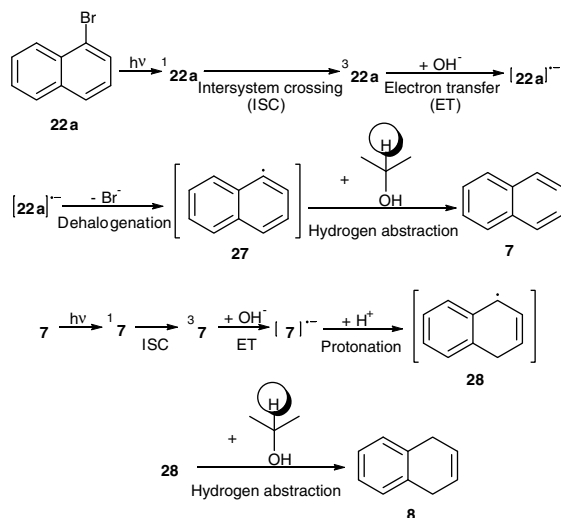
Entry	Haloarenes (10 mM)	Irradn time <sup>a</sup> (h)	Additive	Products (Yield <sup>b</sup> (%))
1	<b>22a</b>	1	—	<b>7</b> (97) <sup>c</sup>
2	<b>22b</b>	1.5	—	<b>10</b> (50)
3	<b>22b</b>	1	<i>t</i> -dodecanethiol 10 mM	<b>10</b> (84)
4	<b>22c</b>	1.5	—	<b>13</b> (77)
5	<b>22d</b>	0.5	—	<b>23</b> (86)
6	<b>22e</b>	1	—	<b>7</b> (84) <sup>c</sup>
7	<b>22f</b>	1	—	<b>7</b> (85) <sup>c</sup>
8	<b>24</b>	1	—	<b>1</b> (59)
9	<b>24</b>	1	<i>t</i> -dodecanethiol 10 mM	<b>1</b> (91)
10	<b>25</b>	1	—	<b>26</b> (94)

<sup>a</sup> Irradiation was carried out with a 100 W high-pressure mercury lamp at room temperature.

<sup>b</sup> Isolated yield.

<sup>c</sup> Determined by GC analysis using authentic sample.

the conventional Birch reaction and dehalogenation using metals, the photoreaction by NaOH could offer many advantages in terms of economical, environmental, and safety standpoints. The investigation of the limitation, application, and detailed mechanism of the photoreaction by the hydroxide ion is currently in progress.



Scheme 1. Plausible mechanism of the photohalogenation and photoreduction.

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### Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.03.123.

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29. After these photoreactions, the mixture was neutralized by 1 M HCl, and the solvent was evaporated. The residue was dissolved in ether, washed with water, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under a reduced pressure to yield the reduction products or the dehalogenated products. These products were isolated by column chromatography on silica gel using hexane and EtOAc as eluents and by preparative HPLC using a GPC column.
30. Excitation of **1** with 40 mM NaOH in 2-PrOH solution for 8 h yielded **2** in 65% isolated yield. The use of KOH and tetrabutylammonium hydroxide instead of NaOH gave **2** in 32% and 41% isolated yields, respectively.
31. Even in the absence of 2-PrOH and cysteine, the photoreaction of **16** (2 mM) with NaOH (500 mM) for 12 h in an aqueous solution afforded **17** in 15% isolated yield, indicating that the hydroxide ion could serve as an electron source for the photoreduction.