



## Convenient Reduction of Azobenzenes and Azoxybenzenes to Hydrazobenzenes by Sodium Dithionite Using Diocetylviologen as an Electron Transfer Catalyst

Kwanghee Koh Park\* and Sun Young Han

Department of Chemistry, Chungnam National University, Taejon 305-764, Korea

**Abstract:** Various azobenzenes and azoxybenzenes were reduced almost quantitatively to the corresponding hydrazobenzenes by sodium dithionite under mild conditions without the formation of aniline derivatives, using dioctyl viologen as an electron-transfer catalyst in acetonitrile-water.  
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Viologens (1,1'-dialkyl-4,4'-bipyridinium,  $V^{2+}$ ) have been utilized as electron-transfer catalysts (ETC) for the reduction of various organic compounds.<sup>1-11</sup> In our previous papers, we reported the viologen-mediated reductive dehalogenation of  $\alpha$ -halogeno ketones,<sup>6</sup> reductive desulfonylation of  $\alpha$ -nitrosulfones,<sup>7</sup> reductive debromination of *gem*-bromonitro compounds,<sup>8</sup> reductive denitration of  $\alpha$ -nitro ketones,<sup>8</sup> reduction of nitroarenes to anilines,<sup>9</sup> reduction of *tertiary* nitroalkanes to hydroxylamines,<sup>10</sup> and reduction of benzoylformic acid to mandelic acid.<sup>11</sup> Here we report convenient reduction of various azobenzenes and azoxybenzenes to the corresponding hydrazobenzenes with sodium dithionite using dioctyl viologen ( $OcV^{2+}$ ) as an ETC in acetonitrile-water. The reaction proceeded almost quantitatively without any overreduction to aniline derivatives.

An aqueous solution (2 ml) of dioctyl viologen (0.04 mmol) was added to a solution of azobenzene<sup>12</sup> or azoxybenzene<sup>14</sup> (0.4 mmol) in acetonitrile (20 ml). To this, an aqueous solution (8 ml) containing  $K_2CO_3$  (0.27 g, 2 mmol) and  $Na_2S_2O_4$  (0.32 g, 1.8 mmol) in case of azobenzenes or an aqueous solution (8 ml) containing  $K_2CO_3$  (0.54 g, 4 mmol) and  $Na_2S_2O_4$  (0.64 g, 3.6 mmol) in case of entry **6b** and azoxybenzenes was added dropwise under a nitrogen atmosphere, and the reaction mixture was stirred at 35 °C. The reaction mixture separated into two phases and a blue color, which is due to the one-electron reduction product of viologen,  $OcV^+$ , persisted in the organic phase until the end of the reaction. After stirring for 0.5-2.5 h, the reaction mixture was extracted with dichloromethane or ethyl acetate. The combined organic layers were dried with anhydrous  $Na_2SO_4$  and treated with silica gel to remove any remaining viologen species, after which tlc showed a single spot except for the case of **6a** (*vide infra*). Since the hydrazobenzenes are easily air-oxidized, the work-up procedures were carried out very cautiously to prevent air exposure. Removal of solvent by flash

evaporation produced the product almost quantitatively, whose  $^1\text{H}$ -nmr spectrum was consistent with the corresponding hydrazobenzene derivative. The results are summarized in the Table.

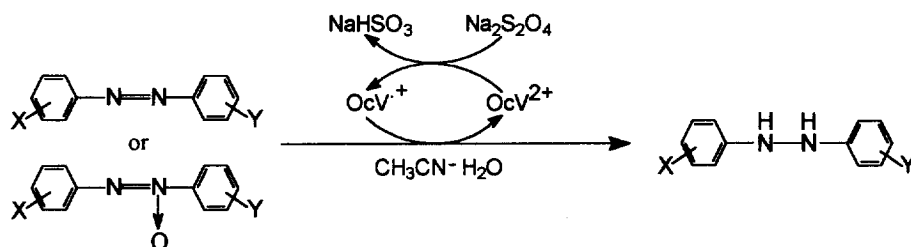
**Table.** Reduction of Azobenzenes and Azoxybenzenes to the Corresponding Hydrazobenzenes with Sodium Dithionite Using Diocetyl Viologen as an Electron-Transfer Catalyst<sup>a</sup>

Entry	Substrate	Time,h	Product	Yield (%) <sup>b</sup>
1a	azobenzene	0.5	hydrazobenzene	96
1b	azobenzene	0.5	hydrazobenzene	61 <sup>c</sup>
2	4,4'-dichloroazobenzene	2.5	4,4'-dichlorohydrazobenzene	96
3	4,4'-dimethylazobenzene	1	4,4'-dimethylhydrazobenzene	92
4	4,4'-dimethoxyazobenzene	1	4,4'-dimethoxyhydrazobenzene	91
5	4-aminoazobenzene	1	4-aminohydrazobenzene	90
6a	4-nitroazobenzene	1	4-nitrohydrazobenzene	62 <sup>d</sup>
6b	4-nitroazobenzene	1.5	4-aminohydrazobenzene	89
7	2,2'-dihydroxyazobenzene	1	2,2'-dihydroxyhydrazobenzene	93
8	azoxybenzene	1	hydrazobenzene	96
9	4,4'-dicyanoazoxybenzene	1	4,4'-dicyanohydrazobenzene	89
10	4,4'-dichloroazoxybenzene	2	4,4'-dichlorohydrazobenzene	96
11	4,4'-dimethoxyazoxybenzene	2	4,4'-dimethoxyhydrazobenzene	91
12	3,3'-diacetylazoxybenzene	2	3,3'-diacetylhydrazobenzene	97

<sup>a</sup> The molar ratio of the viologen to the substrate was 1:10 and the reaction medium was 2:1 (v/v)  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  except for the entry 1b where  $\text{CH}_2\text{Cl}_2$  was used instead of  $\text{CH}_3\text{CN}$ . The molar ratio of the substrate to  $\text{Na}_2\text{S}_2\text{O}_4$  was 1:4.5 for entry 1-6a and 1:9 for entry 6b-12. <sup>b</sup> Isolated yields. <sup>c</sup> Based on  $^1\text{H}$  NMR analysis. <sup>d</sup> In addition to 4-nitrohydrazobenzene in 62 % yield, 4-aminoazobenzene was obtained in 20 % yield.

When the viologen is excluded from the system, no reaction occurs and the starting material is recovered in >95% yield in case of azobenzene derivatives, except for entry 1, 6 and 7. Entry 1 and 7 showed 8 and 77 % conversion based on  $^1\text{H}$  NMR analysis, respectively. In entry 6, most of the starting material was transformed into 4-aminoazobenzene. In case of azoxybenzene derivatives, entry 11 didn't show any conversion in the absence of the viologen, but in other cases, considerable amounts of the corresponding azobenzene and hydrazobenzene were obtained without viologen. The partial direct reduction of some azobenzenes and azoxybenzenes by  $\text{Na}_2\text{S}_2\text{O}_4$  seems to arise from considerable solubility of the substrates in aqueous phase. These results of control experiments clearly indicate that the viologen mediates the reduction, especially for the reduction of the substrates with low water-solubility. Since the molar ratio of the viologen to the substrate is

1:10, the active reductant in the reduction is recycled in the process (Scheme 1).



**Scheme 1** Cyclic pathway for the viologen-mediated reduction of azobenzenes and azoxybenzenes with sodium dithionite

The present results which show the reduction of azobenzenes to hydrazobenzenes without any overreduction to aniline derivatives are noteworthy. Fieser reported that  $\text{Na}_2\text{S}_2\text{O}_4$  reduced an azobenzene, Orange II, to the corresponding aniline derivative.<sup>16</sup> The direct reduction to the aniline derivative by  $\text{Na}_2\text{S}_2\text{O}_4$  might be due to high solubility of the substrate in water and moderately harsh reaction conditions, compared to the conditions employed in this work.

In entry 6, the substrate contains both the azo group and the nitro group. Both groups are reduced to yield 4-aminohydrazobenzene at a longer reaction time with a large excess of  $\text{Na}_2\text{S}_2\text{O}_4$  (entry 6b), but after a shorter reaction time with less amount of  $\text{Na}_2\text{S}_2\text{O}_4$ , 4-nitrohydrazobenzene was obtained in 62 % isolated yield, together with 4-aminoazobenzene in 20 % yield (entry 6a). The reduction of nitro group to amino group by the present procedure is in consistence with our earlier reports.<sup>9,10</sup> During the process of the reduction of azoxy compounds, tlc showed an additional spot corresponding to the azo compound together with the spot of the hydrazobenzene at a shorter time interval, but at a final stage it showed a single spot of hydrazobenzene. This indicates that the reduction of azoxy compounds to hydrazo compounds proceeds *via* azobenzenes. Chloro (entry 2 and 10), cyano (entry 9), and carbonyl (entry 12) groups remain unaffected: this demonstrates clearly mildness and selectivity of the present method.

The reduction reaction proceeded more slowly when the organic solvent was changed from acetonitrile to dichloromethane (compare 1a and 1b). This is reminiscent of our earlier finding<sup>10</sup> that the reduction of an aromatic nitro group to an amino group proceeds at a faster rate in acetonitrile-water than in dichloromethane-water, and an aliphatic nitro group is reduced in the former solvent, but remains intact in the latter medium.

A variety of methods for the reduction of azobenzenes and azoxybenzenes to hydrazobenzenes have been reported and reviewed.<sup>17,18</sup> Most of the classical methods<sup>18</sup> which use reducing reagents such as hydrazine (*via* diimide), lithium aluminum hydride, zinc, and  $\text{H}_2$  (catalytic hydrogenation), and electrochemical reduction<sup>19</sup> can reduce other functional groups. Some of the methods give poor yields, and require strict conditions and/or special apparatus. Several recently developed reagents which include samarium diiodide<sup>20</sup> and aryltelluro<sup>21</sup> for

reduction of azobenzenes to hydrazobenzenes, and dihydrolipoamide-iron(II)<sup>22</sup> and hydrogen telluride<sup>23</sup> for reduction of azo- and azoxy-benzenes to hydrazobenzenes, have been tested only for the parent substances and are rather expensive. In contrast, the present method can be used for the reduction of various substituted azo- and azoxy-benzenes to give the corresponding hydrazobenzenes in almost quantitative yields without affecting other reducible groups such as chloro, cyano, and carbonyl groups. Therefore, this procedure, because of its simplicity, high selectivity, and broad scope, would provide a useful inexpensive alternative route for the reduction of azo- and azoxy-benzenes to hydrazobenzenes.

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