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Sodium Dithionite Reduction of Nitroarenes Using Viologen as an Electron Phase-Transfer Catalyst

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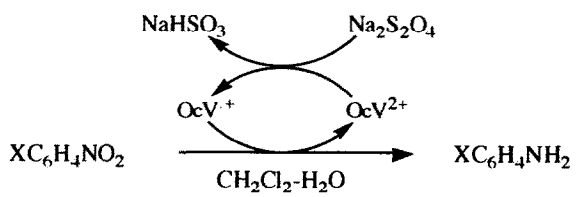
Abstract: Various aromatic nitro compounds were reduced conveniently to the corresponding aniline derivatives with sodium dithionite using dioctyl viologen as an electron-transfer catalyst in dichloromethane- water two-phase system.

Viologens (1,1'-dialkyl-4,4'-bipyridinium, V^{2+}) have received much attention as electron-transfer catalysts (ETC) in photochemical solar energy conversion into hydrogen.[1] Recently, the utilization of viologens as ETCs for the reduction of various organic compounds have been reported.[2-9] In this communication, we wish to report that the nitroarenes are reduced to the corresponding amino compounds almost quantitatively with sodium dithionite using dioctyl viologen ($OcV^{2+}2Br^-$) as an ETC in dichloromethane-water two-phase system.

An aqueous solution (20 ml) containing K_2CO_3 (4.15 g, 30 mmol) and $Na_2S_2O_4$ (4.70 g, 27 mmol) was added dropwise to a mixture of nitroarene (6 mmol) and viologen (0.162 g, 0.3 mmol) in dichloromethane (40 ml)-water (5 ml) under a nitrogen atmosphere. Stirring was continued for 2-8 h at 35 °C and then the aqueous layer was extracted with dichloromethane (3 x 20 ml). The combined organic layers were dried, and treated with silica gel to remove any remaining viologen species, after which tlc showed a single spot. Removal of solvent by flash evaporation produced the corresponding aniline derivative almost quantitatively. The results are summarized in the Table. When the viologen is excluded from the system, no reaction occurs except for entry **1**, **5**, and **7** which showed 18, 5, and 45% conversion based on ^1H NMR analysis. These results clearly indicate that the viologen mediate the reduction. Since the molar ratio of the viologen to the substrate is 1:20, the active reductant in the reduction is recycled in the process (Scheme 1). Under the same reaction conditions, aliphatic nitro compounds such as nitrocyclohexane and 2-nitropropane did not undergo the reduction.



Scheme 1 Cyclic pathway for the viologen-mediated reduction of nitroarenes with sodium dithionite

A complete reduction of a nitro compound would require six electrons, and four-electron reduction would produce a hydroxylamine intermediate[10](eq 1). The reduction of **6** was studied at a shorter time interval. It was found that after 1h reaction time **6** showed ~20% conversion to the hydroxylamine intermediate and ~40% conversion to the aniline derivative and ~40% of **6**

remained unchanged.

$$XC_6H_4NO_2 \xrightarrow[-H_2O]{4e,\ 4H^+} XC_6H_4NHOH \xrightarrow[-H_2O]{2e,\ 2H^+} XC_6H_4NH_2 \qquad (1)$$

Table. Reduction of Nitroarenes to the Corresponding Aniline Derivatives with Sodium Dithionite Using Dioctyl Viologen as an ETC in Dichloromethane-Water Two-phase System.[a]

Entry	Substrate	Time, h	Product	Yield (%)[b]
1	Nitrobenzene	5	Aniline	95
2	3'-Nitroacetophenone	5	3'-Aminoacetophenone	91
3	4-Nitrobenzaldehyde	4	4-Aminobenzaldehyde	96
4	1-Nitronaphthalene	7	1-Aminonaphthalene	91
5	4-Nitrotoluene	2	4-Aminotoluene	97
6	3-Nitrotoluene	3	3-Aminotoluene	94
7	3-Nitrophenol	3	3-Aminophenol	95
8	6-Nitroquinoline	4	6-Aminoquinoline	96
9	8-Nitroquinoline	3	8-Aminoquinoline	95
10	4-Nitrobenzonitrile	3	4-Aminobenzonitrile	92
11	4-Chloronitrobenzene	8	4-Chloroaniline	94
12	3-Nitrostyrene	3	3-Aminostyrene	92

[a] The molar ratio of the viologen to the substrate was 1:20. [b]The isolated yields.

Numerous procedures have been developed to accomplish the reduction of the aromatic nitro compounds, but most of them require relatively expensive catalysts and/or rather harsh reaction conditions. We believe that the procedure described in this paper can be a mild and inexpensive alternative route for the reduction. The mildness of the present method is well demonstrated in the reactions of substrates **2**, **3**, **10**, and **12**, where carbonyl, cyano, and vinyl functional groups are not affected. Further studies on the utilization of the viologen as an ETC for the reduction of different types of organic compounds are in progress.

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REFERENCES

1. Gratzel, M. *Energy Resources through Photochemistry and Catalysis*, Academic Press, New York, NY, 1983.
2. Tomioka, H.; Ueda, K.; Ohi, H.; Izawa, Y. *Chem. Lett.* **1986**, 1359-1362.
3. Maidan, R.; Goren, Z.; Becker, J. Y.; Willner, I. *J. Am. Chem. Soc.* **1984**, *106*, 6217-6222; Endo, T.; Saotome Y.; Okawara, M. *J. Am. Chem. Soc.* **1984**, *106*, 1124-1125.
4. Endo, T.; Saotome, Y.; Okawara, M. *Tetrahedron Lett.* **1985**, *26*, 4525-4526.
5. Saotome, Y.; Endo, T.; Okawara, M. *Macromolecules*, **1983**, *16*, 881-884.
6. Endo, T.; Ageishi, K.; Okawara, M. *J. Org. Chem.* **1986**, *51*, 4309-4310.
7. Park, K. K.; Lee, C. W.; Oh, S.-Y.; Park, J. W. *J. Chem. Soc., Perkin Trans. 1*, **1990**, 2356-2357.
8. Park, K. K.; Lee, C. W.; Choi, S. Y. *J. Chem. Soc., Perkin Trans. 1*, **1992**, 601-603.
9. Park, K. K.; Joung, W. K.; Choi, S. Y. *Bull. Korean Chem. Soc.* **1993**, *14*, 461-465.
10. Mahdavi, F.; Bruton, T. C.; Li, Y. *J. Org. Chem.* **1993**, *58*, 744-746.

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