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Titanium Complex-Catalyzed Borohydride Reduction of Azobenzenes

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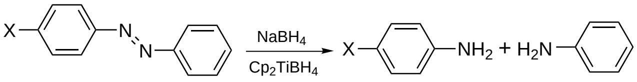
We recently demonstrated that sodium borohydride can be used for titanocene borohydride[1] (Cp_2TiBH_4; **1**)-catalyzed reductive dechlorination of a broad class of noxious haloaromatic substrates,[2] including PCBs[3] and dioxins;[4] this system was even found to be acitve for reduction of PCBs in spiked soils.[3] Nitroorganics are another large category of aromatic organic pollutants that can enter the environment in part as a result of munitions fabrication. Reduction of these nitroorganics should give amines which should, in turn, be readily biodegradable.[5] However, while classical laboratory procedures[6] might be effective for reducing simple nitroorganics in solution, they may not be appropriate for treatment of contaminated environmental substrates, such as soils; approaches to reductive destruction of bulk organics, for example, those based on molten metal technologies,[7] might also be inappropriate in the remediation context. Sodium borohydride reduces nitrobenzene first to azoxybenzene and then to azobenzene,[8] but further reduction to aniline is not efficient with this simple reagent: reduction of azobenzene to 1,2-diphenylhydrazine is slow. We now report that $NaBH_4$ can be used for efficient reduction of azobenzenes to anilines under mild conditions, when catalyzed by **1**.

In a typical procedure, $NaBH_4$ (1.236 g, 32.66 mmol, 6.0 equiv) and Cp_2TiCl_2 (250 mg, 1.00 mmol, 0.185 equiv) were weighed under N_2 and were added to 15 mL of diglyme also under a nitrogen atmosphere (H_2 is evolved). The resulting deep purple solution of **1** was heated to 125 °C, and after 10 min, azobenzene (0.9865 g, 5.420 mmol, 1.0 equiv) and pentadecane (0.40 mL, GC internal standard) in 10 mL of diglyme solution were added by syringe. The reaction mixture turned brown. Aliquots were withdrawn periodically, hydrolyzed, and analyzed by GC. In this way it was found that reduction of azobenzene to aniline occurred with a pseudo-first-order rate constant $k_{obs} = 1.39 \times 10^{-3}$ s^{-1}. A control procedure, omitting **1**, gave an orange solution, and reduction of azobenzene occurred with a pseudo-first-order rate constant $k_{obs} = 2.03 \times 10^{-6}$ s^{-1}. Similarly, reduction of 1,2-diphenylhydrazine was reduced by $NaBH_4$ in the presence of **1** with a pseudo-first-order rate constant $k_{obs} = 2.47 \times 10^{-3}$ s^{-1}; omitting **1**, $k_{obs} = 2.62 \times 10^{-5}$ s^{-1}.

Table 1. Reduction Potentials and Reduction rates for a Series of Azobenzenes



X	reduction potential vs SCE (V)	$E_X - E_H$ (V)	reduction rate k_{obs} (¥ 10^3)	k_X/k_H
CF_3	−1.130	0.202	5.51	3.95
H	−1.332	0	1.39	1
CH_3	−1.396	−0.064	1.21	0.87
OMe	−1.456	−0.124	0.66	0.47
NEt_2	−1.526	−0.194	0.73	0.52

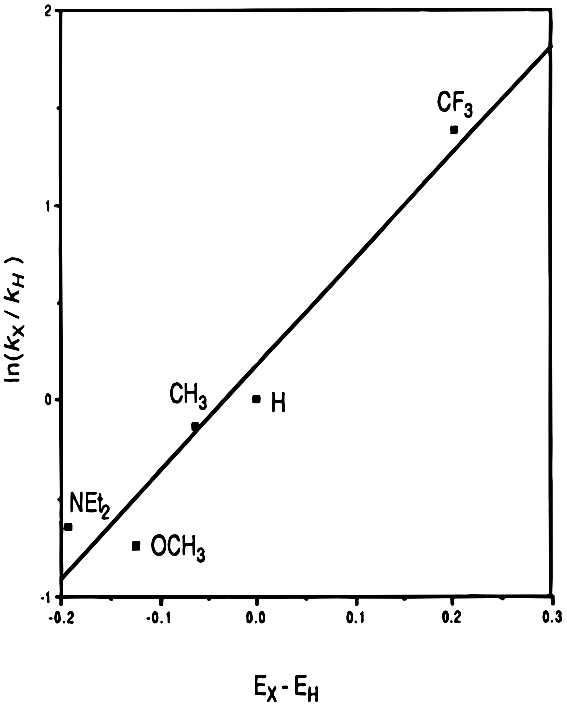
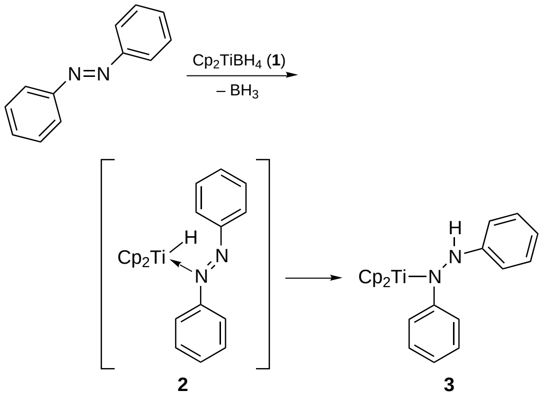


Figure 1. $E_X - E_{[H]}$ *vs* ln (k_X/k_H).

Scheme 1. Reduction of Azobenzene by Coordination and Insertion



Several *p*-substituted substrates (p-$XC_6H_4N{=}NC_6H_4$; X = CF_3,[9] CH_3,[9] OCH_3, NEt_2) were treated with $NaBH_4$. Rates for **1**-catalyzed reduction of each were measured and were correlated with electrochemical reduction potentials measured in THF (Table 1). The correlation observed between relative reduction potentials and re-

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(1) (a) Nöth, H.; Hartwimmer, R. *Chem. Ber.* **1960**, *93*, 2338. (b) Lucas, C. R. *Inorg. Synth.* **1977**, *17*, 91.

(2) Liu, Y.; Schwartz, J. *J. Org. Chem.* **1994**, *59*, 940.

(3) Liu, Y.; Schwartz, J.; Cavallaro, C. L. *Environ. Sci. Technol.* **1995**, *29*, 836.

(4) Liu, Y.; Schwartz, J. *Tetrahedron* **1995**, *51*, 4471.

(5) For an example of facile aerobic degradation of aniline by a *Pseudomonas* strain, see: Konopka, A.; Knight, D.; Turco, R. F. *Appl. Environ. Microb.* **1989**, *55*, 385. Aerobic metabolism of aniline, itself, should be favorable relative to nitrobenzene by arene ring oxidative cleavage. See: Kuznetsov, A. V. *Mol. Biol. (USSR), Engl.* **1991**, *24*, 1096. For measured relative rates, see: Tabak, H. H.; Desai, S.; Govind, R. *44th Purdue Industiral Waste Conference Proceedings*; Lewis Publishers: Chelsea, MI, 1990; p 405.

(6) Fieser, L. F. *Experiments in Organic Chemistry*; D. C. Boston, D. C. Heath: 1963; Chapter 26.

(7) For example, see: Schultz, C. G. *Chem. Abstr.* **1986**, *105*, 48445n.

(8) The reduction of nitrobenzene to azoxybenzene by sodium borohydride in diglyme has been reported. See: Weill, C. E.; Panson, G. S. *J. Org. Chem.* **1956**, *21*, 803.

(9) Ogata, Y.; Takagi, Y. *J. Am. Chem. Soc.* **1958**, *80*, 3591.

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duction rates (*vs* the parent azobenzene; Figure 1) is not inconsistent with a rate-determining electron transfer step for overall reduction. However, in marked contrast to results obtained for aryl halide outer-sphere reduction, which reveal a critical role for added amine,[2] no added amine was required for azobenzene reduction. The reaction between **1** and $^{15}N,^{15}N$-azobenzene was monitored by EPR. The initial signal (at $g = 1.985$; Cp_2TiBH_4) was converted over 6 h to a doublet of doublets ($g = 1.979$; $a_1 = 2.92g$; $a_2 = 5.80g$). A similar spectrum was obtained from the reaction between titanocene borodeuteride and $^{15}N,^{15}N$-azobenzene. Interestingly, the *g* value obtained for the adduct is similar to that recorded for $Cp_2TiOCH(CH_3)(p\text{-}MeOC_6H_4)$ ($g = 1.976$), formed by insertion in a Ti(III)H(*p*-methoxyacetophenone) intermediate.[10] Accordingly, these spectra are assigned to Ti(III) hydrazide complex **3**. We believe, therefore, that azobenzene reduction occurs by initial coordination to Ti(III) as a first step in the reduction process followed by insertion (Scheme 1), as has been found for reduction of ketones by **1**;[11] the rate of insertion in the as yet unobserved adduct **2** would be increased by electron-withdrawing substitution, as was also noted qualitatively for ketone reduction by **1**.[10]

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[10] Barden, M. C.; Schwartz, J. *J. Org. Chem.* **1995**, *60*, 5963.

[11] An η^2-azobenzene adduct is also a possible intermediate.