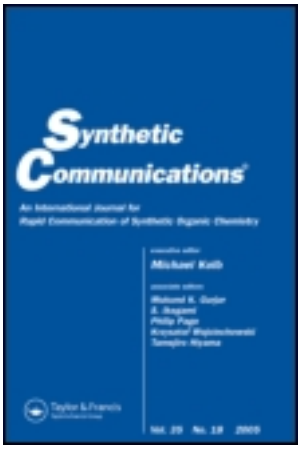

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Uncatalyzed Reductive Fission of Azoarenes to Aminoarene(s) by Hydrazine Hydrate

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Uncatalyzed Reductive Fission of Azoarenes to Aminoarene(s) by Hydrazine Hydrate

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Abstract: Various azoarenes with hydrazine hydrate in refluxing ethanol undergo reductive fission to give easily isolable aminoarene(s) without use of any specialized catalyst. The reaction is fast and cost effective, and yields are excellent (85–95%). Substituents such as —OH, —OCH_3, —COOH, —Cl, and —Br are unaffected. The method affords an elegant route to the preparation of aminoarenes.

Keywords: Aminoarenes, azoarenes, hydrazine hydrate, reductive fission

Previous reports on the reductive cleavage of azoarenes to aminoarenes have been reviewed.[1] The reduction of azoarenes is usually achieved with $HCOONH_4$/10% Pd-C,[2] cycohexene/5% Pd on asbestos,[3] Cp_2TiBH_4,[4] Ni/HCO_2NH_4 or HCOOH,[5] and Zn/HCOOH.[6] More recently, Zn/$CH_3CO_2NH_4$[7] has been reported for the reduction of azoarenes to the

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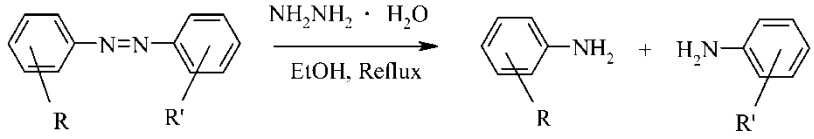
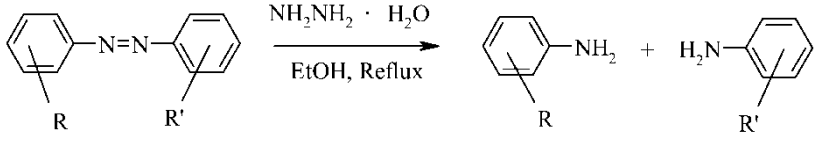


Scheme 1.

corresponding aminoarenes. Some of these procedures use expensive catalysts such as, 5% Pd on asbestos, 10% Pd-C, and so forth. Dehalogenation was observed with $HCOONH_4$/10% Pd-C while benzidine rearrangement with Raney Ni/HCOOH occurred as the reaction proceeded *via* hydrazobenzene intermediate.

It is to be noted that systems such as NH_2NH_2/10% Pd-C[8] and NH_2NH_2/Raney Ni[9] have been reported to convert azobenzene into hydrazobenzene. It is also worth noting that Yu Lu Wang[10] has recently

Table 1. Reduction of azoarenes into aminooarenes by hydrazine hydrate



	Substrate		Product[a]		Yield[b] (%)	
Entry	R	R′	R	R′	1	2
1	H	H	H	H	95	—
2	2-CH_3	2′-CH_3	2-CH_3	2′-CH_3	94	—
3	3-CH_3	3′-CH3	3-CH_3	3′-CH_3	95	—
4	3-OCH_3	3′-OCH_3	3-OCH_3	3′-OCH_3	94	—
5	2-OH	2′-OH	2-OH	2′-OH	90	—
6	2-Br	2′-Br	2-Br	2′-Br	92	—
7	2-Cl	2-Cl	2-Cl	2′-Cl	92	—
8	2-OH	H	2-OH	H	92	94
9	2-COOH	4′-$N(CH_3)_2$	2-COOH	4′-$N(CH_3)_2$	85	92
10	4-COOH	H	4-COOH	H	87	95
11	4-NH_2	H	4-NH_2	H	93	94

[a]Characterized by infrared spectral and on gas chromatographic analysis with authentic samples.

[b]Isolated yields. (Boiling point/melting points were found to coincide with that of authentic samples).

reported the partial reduction of azoarenes using hydrazine hydrate as reducant to get hydrazoarenes in refluxing ethanol after 20 min to 3 h without a catalyst.

In this communication, we demonstrate that 99–100% hydrazine hydrate in refluxing ethanol is a convenient, simple, and chemoselective system for the reductive fission of azoarenes to aminoarenes as shown in Scheme 1.

In a typical experiment 10 mmol of azobenzene and 80 mmol of 99–100% $NH_2NH_2 \cdot H_2O$ in ethanol (20 mL) under reflux for 20–25 min gave aniline (95%). Encouraged by this result, the potential of this reaction was tested for the reductive fission of a variety of azoarenes. The results are summarized in Table 1. The reaction was chemoselective as substituents such as OH, OMe, COOH, Cl, and Br. present on azobenzene derivatives were unaffected.

In conclusion, we have demonstrated for the first time the reductive fission of easily accessible azoarenes by hydrazine hydrate in the absence of any catalysts.

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