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An Eco-Friendly Protocol for the Synthesis of Anilines from Nitroarenes Catalyzed by Zinc and Ammonium Acetate in Aqueous Media

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ABSTRACT

A green methodology for the reduction of substituted nitroarenes to corresponding anilines using ammonium acetate as hydrogen donor and inexpensive commercial zinc dust as catalyst in aqueous media at ambient temperature and pressure is reported. In the Present system, compounds bearing other reducible functional groups like -OH, $-CH_3$, $-OCH_3$, *-COOH,* $-COCH_3$, $-CONH_2$ *and halogens are unaltered. This protocol offers several advantages such as excellent yield, simple procedure, easy work-up and eco-friendly reaction conditions.*

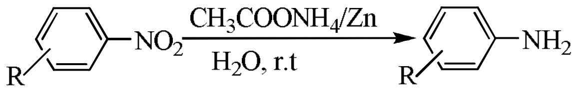
Keywords: Nitroarenes; zinc; ammonium acetate; anilines; aqueous media.

INTRODUCTION

In recent year, organic reactions in aqueous media have received considerable attention. The fact is that water is inexpensive, most abundant, non-toxic and environmentally friendly solvent. It exhibits unique reactivity and selectivity [1]. Replacing organic solvents with water offers economic advantages, improves safety and in combination with the development of catalytic processes offers great opportunities for green chemistry [2].

Synthesis of anilines from substituted nitroarenes is an active and important area of research in organic synthesis [3]. Most of the anilines exhibit biological activities and finds multitude industrial applications, being important intermediates in the synthesis of chemicals such as dyes, antioxidants, photographic, pharmaceutical and agricultural chemicals [4]. Previously, there are many methods available in the literature for the synthesis of anilines from nitroarenes [5-14]. However, these methods suffer from drawbacks like requires expensive and moisture sensitive reagents, unsatisfactory yields and also tedious isolation procedures to remove by-products. Recently, reduction of organic compounds in aqueous medium at high temperature was reviewed in the literature [2, 15 and 16]. However, these reactions require high temperature and prolonged reaction times.

Hence, in this communication, we wish to report a simple, economic and eco-friendly procedure for the reduction of substituted nitroarenes to corresponding anilines by using ammonium acetate as hydrogen donor and inexpensive commercial zinc dust as catalyst at ambient temperature and pressure in aqueous media and the reaction is depicted in **scheme 1**.



R = -OH, -CH$_3$, -OCH$_3$, -COOH, -COCH$_3$, -CONH$_2$ and halogens

Scheme-1

MATERIALS AND METHODS

^{1}H–NMR spectra were recorded on an AMX-400 MHz spectrometer using CDCl$_3$ as the solvent and TMS as internal standard. IR spectra were recorded on Shimadzu FTIR- 8300 spectrometer. The melting points were determined using Thomas–Hoover melting point apparatus and are uncorrected. Thin layer chromatography was carried out on silica gel plates obtained from Whatman Inc. The substrates were either commercial products and were used as purchased or were prepared according to literature procedures. Ammonium acetate and zinc dust (Particle size < 45 µm) was purchased from E-Merck Mumbai (India) Ltd., Mumbai. All the solvents used were of analytical grade or were purified according to standard procedures.

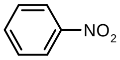
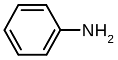
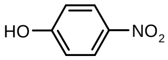
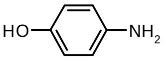
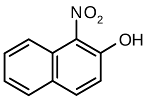
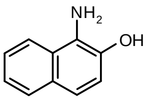
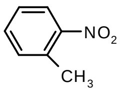
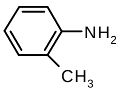
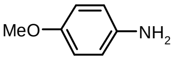
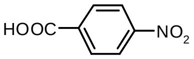
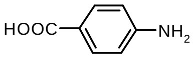
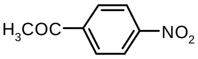
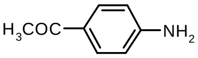
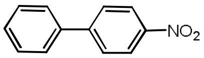
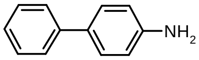
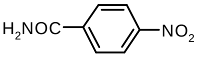
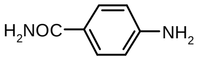
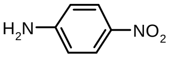
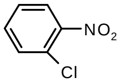
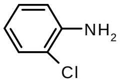
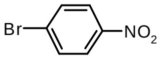
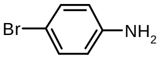
General procedure for the synthesis of anilines from nitroarenes: A suspension of nitroarene (10 mmol) and commercial zinc dust (10 mmol) in water (15 mL) was stirred with ammonium acetate (20 mmol) at room temperature. The reaction was exothermic. After completion of the reaction (monitored by TLC), the product was extracted with Et$_2$O or CH$_2$Cl$_2$ (2 x 30 mL). The extract was washed twice with saturated sodium chloride solution (30 mL) and then with water (30 mL). The organic layer was dried over anhydrous Na$_2$SO$_4$ and the solvent was evaporated under reduced pressure to obtain the desired products.

RESULTS AND DISCUSSION

This new system reduced a wide range of structurally varied nitroarenes to anilines in excellent yield. Many other reducible functional groups like -OH, -CH$_3$, -OCH$_3$, -COOH, -COCH$_3$, -CONH$_2$ and halogens were tolerated. All the nitroarenes were easily reduced to their corresponding anilines by using ammonium acetate and inexpensive commercial zinc dust in aqueous media at ambient temperature and pressure and are listed in table 1. It is worth to note that all the nitroarenes reduced by this system were obtained in excellent yields (90-95%). The reactions are extremely easy to carryout and completes within 5 to 10 min. The course of reaction was monitored by thin layer chromatography and IR spectra. The work-up and isolation of the products were easy. All the products were characterized by m.p., IR and ^{1}H-NMR techniques followed by comparison with authentic samples. The yields are virtually quantitative and analytically pure.

A control experiment was carried out by using substituted nitroarenes with ammonium acetate but without zinc dust, which did not yield the desired product. Furthermore, an attempted reduction of substituted nitroarenes using zinc dust in the absence of ammonium acetate which did not yield the desired product even if the reaction mixture was stirred for more than 24h.

Table 1: A facile and eco-friendly protocol for the synthesis of anilines from nitroarenes catalyzed by zinc and ammonium acetate in aqueous media

					Melting Point °C	
	Nitro compounds	Time (min)	Anilines	Yield[a] (%)	Found	Lit.
1		10		90[b]	182-185	184-186[17]
2		5		92	187-188	189[17]
3		8		93	204-207	206[17]
4		5		91[b]	200-202	200-202[18]
5		6		90	58-60	57[17]
6		10		92	184-186	187[17]
7		8		93	103-105	106[18]
8		5		90	135-137	137[17]
9		8		90	115-116	114[17]
10		5		95	140-143	141[17]
11		5		95[b]	107-109	108[18]
12		6		90	66-67	66[18]

All the products are known and the isolated products gave ^1H NMR and IR data which are in good agreement with their structures. [a]Isolated yields are based on single experiment and the yields were not optimized. [b]Boiling point.

APPLICATIONS

This method offers an economical, safe, and environmentally benign alternative to available procedures with excellent yield, simple procedure, easy work-up and short reaction time.

CONCLUSIONS

In conclusion, we have reported a facile method for the synthesis of anilines from nitroarenes catalyzed by inexpensive commercial zinc dust and ammonium acetate as hydrogen donor in aqueous media. The catalyst is non-pyrophoric in nature and another interesting behavior of Zn dust lies in the fact that it can be recycled after simple washing with Et_2O and dil. HCl, thus rendering the process more economic. In this reduction process, water, apart from being a green solvent, effectively controls the rate of the reaction and hence exothermicity. The limited solubility of the substrate in water maintains sufficient productivity and also prevents reaction runaway. The present method offers an economical, safe, and environmentally benign alternative to available procedures with excellent yield, simple procedure, easy work-up and short reaction time.

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