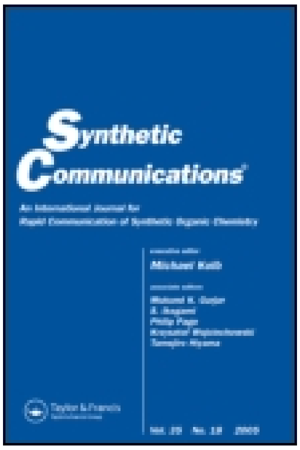

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# Reductive Cleavage of Azo Compounds by Zinc and Ammonium Chloride

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# Reductive Cleavage of Azo Compounds by Zinc and Ammonium Chloride

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## ABSTRACT

Azo compounds are reduced to corresponding anilines with zinc dust in the presence of ammonium chloride in methanol at room temperature.

*Key Words:* Azo compounds; Reductive cleavage; Ammonium chloride; Zinc dust; Anilines.

## INTRODUCTION

Reductive cleavage of azo compounds is a key step in organic chemistry. Numerous reagents have been developed for the reductive cleavage of azo

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compound to anilines.[1–6] However, these methods suffer from one or more limitations. Currently, we wish to report our novel observation on the ammonium chloride mediated reductive cleavage of azo compounds to corresponding anilines in the presence of low cost zinc dust (Sch. 1).

The reduction of azo compounds to corresponding anilines in the presence of zinc dust and ammonium chloride was completed within 5–20 min at ambient temperature. The course of reaction was monitored by thin layer chromatography and IR spectra. The reduced products were obtained in good yields and the products were characterized by comparison of their melting points, TLC, and IR spectra with authentic samples. The disappearance of a strong absorption band between 1630 and 1575 $cm^{-1}$ due to the –N═N– stretching and the appearance of a strong absorption band between 3500 and 3300 $cm^{-1}$ due to the $-NH_2$ group clearly showed that the azo compounds had been cleaved into their substituted anilines. Table 1 showed that many functional groups such as $OCH_3$, OH, COOH, $CH_3$, $COCH_3$, $SO_3Na$, and halogens are tolerated during the cleavage step.

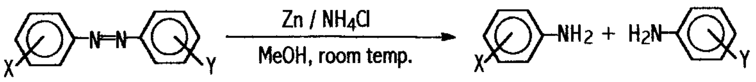
A control experiment was carried out using azo compounds with ammonium chloride, in the absence of zinc, the formation of anilines could not be detected. Methanol was found to be the best solvent.

In summary, this article describes a simple protocol to cleaved azo compounds in their corresponding anilines with good yields in the presence Zn-$NH_4Cl$.

## EXPERIMENTAL

### Materials

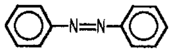
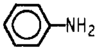
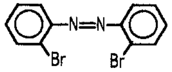
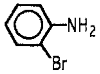
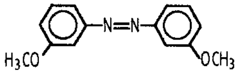
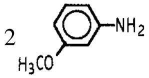
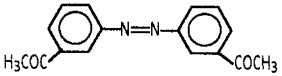
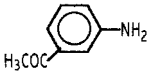
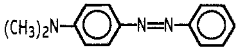
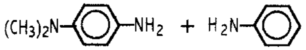
Azo compounds were purchased from Aldrich Chemical Company (Sigma-Aldrich, UK) or prepared according to standard procedures reported earlier.[9] All of the solvents used were analytical grade or were purified according to standard procedures. Thin layer chromatography was carried out on silica gel plates obtained from Whatman Inc. The melting points



X or Y = -H, halogen, -OH, -$OCH_3$, -COOH, -$COCH_3$,-$CH_3$

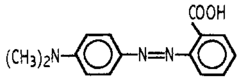
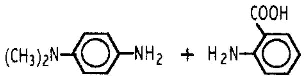
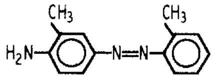
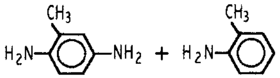
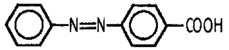
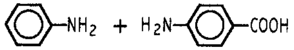
*Scheme 1.*

***Table 1.*** Reduction of azo compounds to anilines by using zinc and ammonium chloride.[a]

| Entry | Substrate | Product | Time (min) | Yield (%)[b] | $R_f$ values | Melting point (°C) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Found | Literature |
| 1 |  | 2  | 5 | 95[d] | 0.39 ($R_f^1$) | 112 | 114[7] |
| 2 |  | 2  | 7 | 92[c] | 0.69 ($R_f^1$) | 115 | 116[7] |
| 3 |  | 2  | 10 | 92[d] | 0.64 ($R_f^2$) | 78 | 80[7] |
| 4 |  | 2  | 12 | 91 | 0.61 ($R_f^2$) | 100 | 99[7] |
| 5 |  |  | 15 | 90[d],<br>92[d] | 0.24, 0.91 ($R_f^3$) | 50, 112 | 53,[8] 114[7] |

(*continued*)

*Table 1.* Continued.

| Entry | Substrate | Product | Time (min) | Yield (%)[b] | $R_f$ values | Melting point (°C) | |
|---|---|---|---|---|---|---|---|
| | | | | | | Found | Literature |
| 6 |  |  | 20 | 88[d], 80[e] | 0.30, 0.68 ($R_f^4$) | 52, 144 | 53,[8] 145[7] |
| 7 |  |  | 15 | 90, 93[c] | 0.51, 0.65 ($R_f^2$) | 62, 144 | 64,[7] 144[7] |
| 8 |  |  | 18 | 90, 75[d,e] | 0.82, 0.30 ($R_f^2$) | 113, 188 | 114,[7] 186[7] |

*Note:* In the case of unsymmetrical azo compounds, the first number refers to the X-substituted fragment and the second number refers to the Y-substituted fragment of the reductively cleaved azo compound.

[a] More than 15 azo compounds are reductively cleaved, only representative examples are given.

[b] Isolated yields are based on single experiment and the yields were not optimized.

[c] Isolated as benzoyl derivative.

[d] Isolated as acetyl derivative.

[e] The low yield is due to its water-soluble nature; TLC analysis indicates complete cleavage.

were determined by using a Thomas–Hoover melting point apparatus and are uncorrected. IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer.

### Typical Procedure

A suspension of the azo compound (10 mmol) and zinc dust (10 mmol) in methanol (15 mL) or suitable solvent (15 mL) and ammonium chloride (20 mmol) was stirred under a nitrogen atmosphere at room temperature. After the completion of the reaction (monitored by TLC) the reaction mixture was filtered through a Celite pad and washed with solvent. The combined filtrate and washings were concentrated, the residue dissolved in chloroform (30 mL) or diethyl ether and washed with saturated brine solution (30 mL × 2) and water. The organic layer was dried over anhydrous magnesium sulfate and concentrated. The residue was purified by preparative TLC or silica gel chromatography.

## ACKNOWLEDGMENT

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