Reduction of nitrosoarenes into anilines by Al/NH₄Cl in refluxing methanol

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A simple, cost-effective method for the reduction of nitrosoarenes by aluminium in the presence of ammonium chloride in refluxing methanol to give anilines is reported.

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The reduction of nitrosoarenes into anilines is an important reaction in organic synthesis and is an active area of research for many years. A number of reagents like, Zn, Sn/HCl,² hydrogenation over platinum,³⁻⁴ nickel,⁵ palladium,⁶ and other catalysts,⁷ have been used to bring about this conversion under various reaction conditions. Sodium bisulphite reduces p-nitrosotoluene to p-toluidine and also sulfonates the ring.⁸ Enzymatic reduction of p-nitrosobenzoic acid to p-aminobenzoic acid has been observed.⁹ Sodium alcoholates,¹⁰ NaBH₄·CH₂OH·CH₃ONa,¹⁰ are known. Selective reduction of nitrosoarenes with Bakers yeast has also been reported.¹¹

Some of the above methods have significant limitations based on safety and handling considerations. The most common methods employed for the reduction of nitrosoarenes are catalytic hydrogenation and catalytic transfer hydrogenation. However, metals like palladium and Raney nickel used for this purpose are flammable in the presence of hydrogen gas or a hydrogen donor when exposed to air, and in many cases, the method demands elevated temperatures or expensive reagents.

Recently, we have reported the selective reduction of nitroarenes¹² and arylhydroxyl amines,¹³ into the corresponding anilines by Al/NH₄Cl. In continuation of our work on utilization of aluminium metal for the reduction of different functional groups,¹²⁻¹⁶ and to establish the mechanism of reduction of nitroarenes by Al/NH₄Cl, we have examined the reduction of nitrosoarenes under identical conditions.

In this paper, we report the results of the reduction of nitrosoarenes to the corresponding anilines using Al metal in the presence of NH₄Cl in refluxing methanol (Scheme 1).

\[
\text{R-NO} \xrightarrow{\text{Al/NH}_4\text{Cl, reflux}} \text{R-NH}_2
\]

Scheme 1

Nitrosoarenes give respective anilines in excellent yields when treated with Al/NH₄Cl in refluxing methanol (Table 1). As mentioned earlier,¹²⁻¹３ Al metal alone did not give the product. In the presence of NH₄Cl, the reaction went to completion within 5 hr in certain cases. However, compounds such as nitrobenzene and 1-nitroso-2-naphthol took longer time for complete reduction. Exposure to ultrasound (bath working at 35 KHz) increased the rate of the reaction by two folds and the yields of the products were 5–10% higher than in the experiments that were performed at reflux temperature of the solvent.¹⁴ As aluminium metal and NH₄Cl are readily available, the method is simple, convenient and economically viable which can be used to synthesize a number of simple as well as substituted anilines from nitrosoarenes. As nitrosoarenes and arylhydroxyl amines give anilines under these reaction conditions in high yields, it is

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<th>Table 1—Reduction of nitrosoarenes to corresponding anilines using Al/NH₄Cl in methanol</th>
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expected that the reduction of nitroarenes proceeds through the intermediacy of nitrosoarene intermediates (Scheme II).

\[
\begin{align*}
R-\text{NO}_2 & \xrightleftharpoons{\text{AlNH}_2\text{Cl}\text{, MeOH, reflux}} R-\text{NO} \xrightarrow{\text{AlNH}_2\text{Cl}\text{, MeOH, reflux}} R-\text{NH}_2 \\
R = \text{aryl}
\end{align*}
\]

Scheme II

Experimental Section

All the nitrosoarenes were prepared by the standard procedures. Purification was done by recrystallisation from light pet. ether (40-60°C), and characterised from their IR spectral analysis (Nicolet 400 FT-IR). Yield refers to the isolated products of >95% purity. JULABO, USR-3 German-make sonic bath was used to check the reaction under sonic conditions.

Reduction of nitrosoarenes: General procedure

A mixture of nitrosobenzene (1.07 g, 10 mmole) and NH₂Cl (160 mg, 30 mmole) in methanol (10 mL) was stirred on a preheated oil-bath, while maintaining the temperature between 60 and 65°C. The reaction was initiated through the addition of aluminium foil (82 mg, 30 mg atom cut into small pieces). The progress of the reaction was monitored by TLC [5% acetone : pet. ether (40-60°C)]. At the end of the reaction, the contents were cooled to room temperature, filtered, washed successively with acetone (3 × 10 mL), and the filtrate was dried over anhydrous Na₂SO₄. The solvent was evaporated to afford the crude product which was then chromatographed over basic alumina using 5% acetone : pet. ether (40-60°C) to yield pure aniline (85%) (Table I).

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References