

REDUCTION OF ARYL NITRO COMPOUNDS WITH ALUMINIUM / NH_4Cl : EFFECT OF ULTRASOUND ON THE RATE OF THE REACTION

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Abstract: Aromatic nitro compounds undergo smooth reduction when treated with aluminium and ammonium chloride in refluxing methanol to give anilines in high yield. The reaction rate is greatly enhanced by irradiating at 35 KHz in a sonic bath at 25°C. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Chemical ultrasonics began in 1927 when the acceleration of a conventional reaction was reported by Richards and Loomis.¹ Since then, a number of chemical reactions have been observed in an ultrasonic field.²⁻⁴ Sonic conditions not only accelerates chemical reactions, it reduces the number of steps which are required using normal conditions, cruder reagents can be used and reactions can be initiated without any additives. The chemical effects of ultrasound are due to the phenomenon of acoustic cavitation.⁵ The primary chemical reactions result from a transient state of high temperatures and pressures.⁶

The conversion of aromatic nitro compounds into anilines is an important reaction in organic synthesis. A number of reagents have been previously known to bring about this conversion under various reaction conditions among them Sn, Zn or Fe/aqueous HCl, $\text{AlH}_3\text{-AlCl}_3$ -hydrazine,⁷ TiCl_3 ,⁸ formic acid/ Pd-C ,⁹ ammonium formate/ Pd-C ,¹⁰ sulfides or polysulfides,¹¹ sodiumtrimethylsilane thiolate,¹² CO/H_2 catalysed by $\text{Ru}_3(\text{CO})_{12}$,¹³ NaBH_4 and SbCl_3 or BiCl_3 ¹⁴ or $\text{CH}_3\text{OH-CH}_3\text{ONa}$,¹⁵ $\text{KBH}_4\text{-BiCl}_3$,¹⁶ samarium/ $(\text{CH}_3)_3\text{SiCl/NaI}$,¹⁷ potassium selenated borohydride¹⁸ and Pd-cat under the influence of ultrasound¹⁹ are used for this purpose.

In this paper we present the results of an investigation of the reaction of aryl nitro compounds with aluminium metal in presence of ammonium salts in refluxing methanol. The results listed in Table-1 confirm that the reaction is possible only with ammonium chloride, and the reaction takes a long time for completion. However, under the influence of ultrasound at 35 KHz the reaction is appreciably faster.

Table 1 : Reduction of Nitrobenzene with Aluminium in presence of Ammonium salts in Methanol.

Entry	Al + Ammonium Salt	At reflux	Product	yield %
1	Aluminium alone	No reaction	No reaction	-
2	NH_4Cl	24 hours	Aniline	90
3	NH_4NO_3	No reaction	No reaction	-
4	$(\text{NH}_4)_2\text{SO}_4$	No reaction	No reaction	-
5	NH_4COOH	No reaction	No reaction	-
6	$(\text{NH}_4)_2(\text{COO})_2$	No reaction	No reaction	-
7	$\text{NH}_4\text{OCOCH}_3$	No reaction	No reaction	-

The facile reduction of different nitro compounds into respective anilines under the influence of ultrasound is noteworthy (Table -2). The method is simple, convenient and cost effective as the reagents are readily available. Reaction of aryl nitro compounds with aluminium in presence of ammonium chloride is expected to proceed *via* single electron transfer mechanism. As aluminium metal alone is non-reactive (Table-1, entry-1) and only ammonium chloride initiates the reaction (entry-2), ammonium chloride is expected to participate in the reaction.

Table 2 : Reduction of Aryl nitro compounds using Aluminium/Ammonium Chloride.

Entry	Substrate	Products	Duration (in hr)		Yield %	m.p. or b.p. °C
			Under reflux	At 35 KHz in a sonic bath (25°C)		
1.	Nitrobenzene	Aniline	24	2	75	178
2.	4-Chloronitrobenzene	4-Chloroaniline	22	1	80	68
3.	2-Chloronitrobenzene	2-Chloroaniline	20	2.30	70	202
4.	3,4-dichloro nitrobenzene	3-4-dichloroaniline	18	2.15	75	70
5.	1,3-dinitrobenzene	1,3-phenylene diamine	22	1.15	70	64
6.	2-nitrotoluene	2-Toluidine	6	1.50	72	194
7.	4-nitroaniline	1,4-phenylene diamine	24	2.0	90	143
8.	2-nitroaniline	1,2-phenylene diamine	26	2.15	85	103
9.	4-nitrophenol	4-aminophenol	36	3.00	86	178
10.	2-nitrophenol	2-aminophenol	30	2.30	90	174
11.	3-nitrobenzoic acid	3-aminobenzoic acid	8	1.30	70	188
12.	2-nitrobenzoic acid	Anthranilic acid	7	1.45	75	144

Experimental : All compounds were characterised by direct comparison on tlc with authentic samples. Yield refers to the isolated products of >95% purity. All the reactions were studied using JULABO, USSR-3 GERMAN make sonic bath working at 35 KHz (constant frequency) at 25°C.

Reaction of Aryl nitro compounds at 35 KHz : General Procedure:- A mixture of nitro benzene (123mg, 10 mmol) aluminium foil (82mg, 30mg atom cut into small pieces) and ammonium chloride (160mg, 50 mmol) in methanol (10 ml) was sonicated at 35 KHz in a sonic bath maintained at 25°C. The progress of the reaction was monitored by tlc (5% Me₂CO:hexane). At the end of the reaction, the contents were filtered, washed successively with ether (3x15 ml) and then with acetone (2x15 ml), the filtrate was dried (sodium sulphate) and evaporated to remove the solvent. The product was chromatographed over basic alumina using 5% Me₂CO: hexane to yield pure aniline (70mg, 75%). The yield and physical constants of different anilines are given in the Table-2.

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