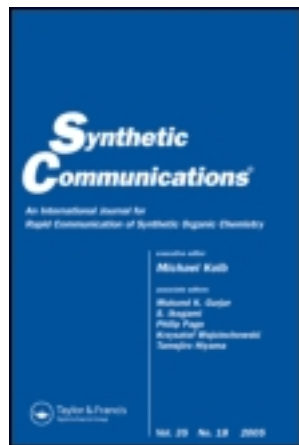


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### A SIMPLE AND CONVENIENT METHOD FOR THE REDUCTION OF NITROARENES\*

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## A SIMPLE AND CONVENIENT METHOD FOR THE REDUCTION OF NITROARENES\*

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### ABSTRACT

A variety of nitroarenes such as simple, electron rich and electron poor were reduced on Al<sub>2</sub>O<sub>3</sub> support in presence of sodium hydrogen sulphide under microwave condition to give the corresponding aromatic amines in high yields. It is found that the substituents at different positions on nitrobenzene have no influence except **2d** on the rate of reaction and yields of product.

In general the aromatic amines are considered to be important intermediates in the synthesis of a number of nitrogen heterocycles. Some of them are used in dyes,<sup>[1]</sup> drugs,<sup>[2]</sup> pharmaceuticals,<sup>[3]</sup> pesticides<sup>[4]</sup> and so on. The synthesis of these compounds is mainly from nitroarenes by way of

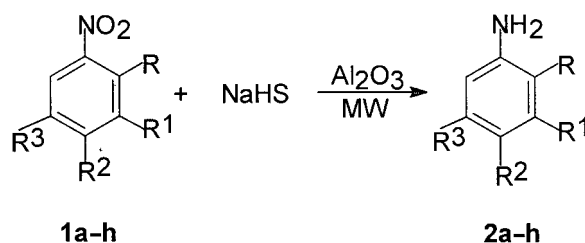
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reduction, however a few examples are from other precursors. Earlier methods on the reduction of nitro compounds using sodium sulphide,<sup>[5]</sup> hydrogen sulphide on Fe<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>,<sup>[6]</sup> sodium hydrogen sulphide,<sup>[7]</sup> phase transfer catalyst,<sup>[8]</sup> heterogenous catalyst,<sup>[9]</sup> Mg salts<sup>[10]</sup> have been reported. However all the methods are of specific in nature. The development of an efficient and universally applicable method for the synthesis of aromatic amines is of current interest. We wish to report here for the first time a simple and convenient method for the reduction of variety of aromatic amines.

In continuation of our interest<sup>[11]</sup> on the development of new and efficient methodology for important products, we have further developed that in a typical experiment, the nitrobenzene was reduced on alumina support in presence of sodium hydrogen sulphide under microwave irradiation conditions and obtained aniline. It is learned from literature<sup>[12]</sup> that the reduction of nitrobenzene with sodium hydrogen sulphide results in phenyl hydroxylamine and further reduction to aniline. The initial reduction to phenyl hydroxylamine seems to be faster than followed reaction. In order to see the effect of substituent on the rate of reaction, a number of substituted nitrobenzenes have been chosen for study. Thus the method was applied to the reduction of substituted nitrobenzenes having electron donating groups (CH<sub>3</sub>, NH<sub>2</sub>, OH) and electron withdrawing groups (CHO, Cl, F, CF<sub>3</sub>) to result in the corresponding anilines. We found that the substituents have no effect except **2d** on the rate of reaction and yields of product. In addition, the developed method has advantage of shorter reaction times, with high yields and neat isolation of products. Alternately the same reaction in case of **2b** and **2e** were carried out in thermal conditions for 10 h and yields were found to be low. The products have been characterized based on their IR, <sup>1</sup>H NMR and mass spectra and comparing with the data available in literature. The reaction has been formulated in the Scheme 1 below.



Scheme 1.



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Table 1.

Entry	Compound			Reaction Time (min)	Yield (%)	M.P.(°C)		
	No	R	R <sup>1</sup>			Rec.	Lit.	
1	<b>2a</b>	H	H	H	4	95	–	–
2	<b>2b</b>	H	H	CH <sub>3</sub>	4	90	43–45	44–46 <sup>[13]</sup>
3	<b>2c</b>	H	H	NH <sub>2</sub>	4	95	138–140	141–143 <sup>[14]</sup>
4	<b>2d</b>	H	H	OH	2	70	192–194	190–192 <sup>[15]</sup>
5	<b>2e</b>	H	H	CHO	4	85	76–78	74–75 <sup>[16]</sup>
6	<b>2f</b>	H	Cl	Cl	4	80	66–68	68–70 <sup>[17]</sup>
7	<b>2g</b>	H	Cl	F	4	75	46–48	45–47 <sup>[18]</sup>
8	<b>2h</b>	Cl	H	H(R <sup>3</sup> = CF <sub>3</sub> )	4	90	–	–

The number of products synthesized have been tabulated in Table 1.

## EXPERIMENTAL

Melting points were determined in open glass capillaries on a Fisher-Johns melting point apparatus and are uncorrected. IR spectra were recorded on FT-IR Shimadzu Perkin-Elmer 1310 infrared spectrophotometer. <sup>1</sup>H NMR spectra were recorded on Varian Gemini (200 MHz) spectrometer and TMS was used as internal standard. Mass spectra were recorded on a VG-micromass 7070H instrument at 70 eV.

## GENERAL PROCEDURE

**(a) Preparation of the Reagent:** Dissolved 0.01 moles of crystallised sodium sulphide (Na<sub>2</sub>S·9H<sub>2</sub>O) in 10 mL of water and added 0.01 moles of finely powdered NaHCO<sub>3</sub> in small portions with constant stirring. When the carbonate has dissolved completely, added 10 mL methanol and cooled below 20°C. Filtered off the precipitated sodium carbonate using Buchner filter, washed the precipitate with methanol. The resulted filtrate was adsorbed on alumina and dried.

**(b) Reaction Procedure:** Dissolved 0.004 moles of nitro compound in ether and adsorbed on the above prepared reagent and after drying subjected to microwave irradiation (600 W, BPL BMO 700T) for 2–4 min. Then it is cooled to room temperature and purified through a silica gel column. The product aniline is eluted with 50% hexane–chloroform.



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