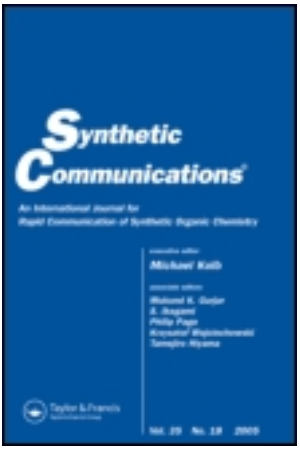

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

FeS-NH_4Cl-CH_3OH-H_2O: AN EFFICIENT AND INEXPENSIVE SYSTEM FOR REDUCTION OF NITROARENES TO ANILINES*

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Published online: 09 Nov 2006.

To cite this article: D. G. Desai , S. S. Swami , S. K. Dabhade & M. G. Ghagare (2001) FeS-NH_4Cl-CH_3OH-H_2O: AN EFFICIENT AND INEXPENSIVE SYSTEM FOR REDUCTION OF NITROARENES TO ANILINES* , Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:8, 1249-1251, DOI: 10.1081/SCC-100104012

To link to this article: http://dx.doi.org/10.1081/SCC-100104012

SYNTHETIC COMMUNICATIONS, 31(8), 1249–1251 (2001)

$FeS\text{-}NH_4Cl\text{-}CH_3OH\text{-}H_2O$: AN EFFICIENT AND INEXPENSIVE SYSTEM FOR REDUCTION OF NITROARENES TO ANILINES*

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ABSTRACT

Nitroarenes are reduced to corresponding anilines with $FeS\text{-}NH_4Cl\text{-}CH_3OH\text{-}H_2O$ system in good yields.

Although a number of reagents are available in the literature for reduction of different functional groups, the development of mild, neutral, and selective reducing systems still attracts a great deal of attention of organic chemists. In recent years, reagents based on iron find wide application in organic synthesis because of their ready availability, ease of handling, and low cost. Reduction of nitroarenes to anilines is an important reaction in organic chemistry. We report here the same using $FeS\text{-}NH_4Cl\text{-}CH_3OH\text{-}H_2O$ system in good yields (Tab.).

Reduction of nitroarenes to anilines mediated by zinc has been achieved by several systems[1–4] such as Zn-HCl, Zn-NaOH, $Zn\text{-}NH_4Cl$,

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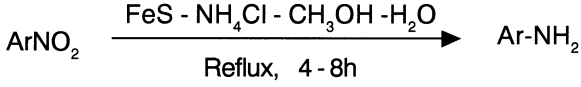
and Zn-$CaCl_2$, but each has drawbacks. For example, Zn-HCl system is not suitable for nitro compounds with acid-sensitive functionalities like amino group, and it also produces hazardous chloronitro compounds. Zn-NH_4Cl system gives toxic phenyl hydroxylamines as major products. The other systems, Zn-NaOH and Zn-$CaCl_2$-H2O, require stringent reaction conditions. Besides zinc-mediated reduction of aromatic nitro compounds, several other systems have also been reported using different reagents:[5–12] $NaBH_4$; Sn-HCl; Fe-HCl; and catalytic reduction using Pt or Pd/C. The low yields, costly chemicals, stringent reaction conditions, and tedious work-up are the major drawbacks of the above systems. This prompted us to apply FeS-NH_4Cl - CH_3OH-H_2O system (Scheme) for reduction of nitroarenes to anilines. The chemicals required for this system are easily available, cheap, and nontoxic. The present system is mild, neutral, eco-friendly, and a useful addition to the existing systems to convert nitroarenes to anilines.



Scheme 1.

The following compounds were prepared in the laboratory (Table). The progress of the reaction was monitered by TLC and products were characterized by comparison with authentic samples,[13] suitable derivatization, and spectral analysis (IR and PMR). The reduction of polynitroarenes using the above system is in progress.

Table. Reduction of Nitroanilines to Anilines

Entry	Nitroarenes	Product	Time (h)	Yield (%)	M.p./[b.p.] °C
1.	Nitrobenzene	Aniline	4	81	[184]
2.	*p*-Nitrotoluene	*p*-Toludine	5	74	44–45
3.	α-Nitronaphthalene	α-naphthylamine	6	78	50–51
4.	*p*-Nitrobenzoic acid	*p*-Aminobenzoic acid	5	76	186–187
5.	*o*-Nitrophenol	*o*-Aminophenol	8	56	173–174
6.	*p*-Nitrophenol	*p*-Aminophenol	5	74	185–186
7.	*p*-Nitroaniline	*p*-phenylene diamine	6	76	142
8.	*m*-Nitroaniline	*m*-phenylene diamine	6	72	64
9.	*p*-Chloronitrobenzene	*p*-Chloroaniline	5	77	69–70
10.	*N*-Benzyl-m-nitro aniline	*N*-Benzyl-m-phenylene diamine	6	75	57–58
11.	Methyl-*p*-nitro benzoate	Methyl-*p*-amino benzoate	5	80	108

EXPERIMENTAL

General Procedure for Reduction

Nitrocompound (10 mmole) was dissolved in a mixture of methanol (40 mL) and water (10 mL). To this commercial powdered iron sulphide (50 mmole) and ammonium chloride (50 mmole) were added. It was refluxed in a water bath (TLC monitering, see Table). When the reaction was over, residue was filtered, washed with methanol (2×5 mL), and basified by adding a saturated solution of sodium carbonate. Solvent was removed by distillation under reduced pressure, and residue was extracted with methylene chloride (3×30 mL). The combined organic layer was washed with water (2×25 mL) and dried over potassium hydroxide pellets. Removal of solvent under reduced pressure furnished aminocompound, which was further purified by distillation or crystallization from water or water–alcohol mixture.

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Accepted July 7, 2000