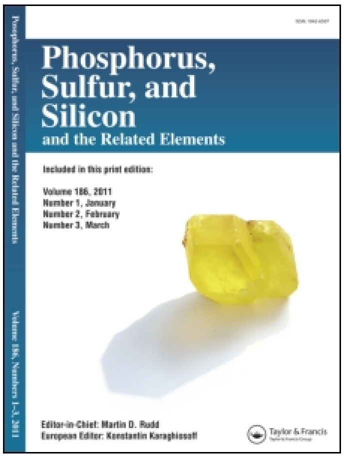

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# Efficient Reduction of Nitroarenes to the Corresponding Anilines with Sulfur in Basic Media under Solvent-Free Conditions

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# EFFICIENT REDUCTION OF NITROARENES TO THE CORRESPONDING ANILINES WITH SULFUR IN BASIC MEDIA UNDER SOLVENT-FREE CONDITIONS

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*Aromatic nitro compounds can be conveniently reduced to the corresponding primary amines in the presence of $S_8$ under solvent-free conditions in excellent yields. Alumina supported NaOH catalyses this transformation. Chemoselectivity was observed in the reduction of the nitro group in the presence of phenol, carboxylic acid, aldehyde, and benzyl halide groups.*

*Keywords:* Alumina supported NaOH; chemoselectivity; nitroarens; reduction; sulfur

Aromatic amines are used widely as intermediates for dyes, photographic materials, pharmaceutical chemicals, agricultural chemicals, and antioxidants. Further, the primary aromatic amines are converted readily into diazonium salts, which can be substituted for many other functional groups. In spite of numerous methods available, the reduction of nitroarenes to primary amines is of practical importance and the development of efficient and reliable reagents for this propose has been an objective of synthetic chemists.[1] It is usually accomplished by means of catalytic hydrogenation,[2] metal, and acids,[3] hydride reagents,[4] $NaBH_4$- transition metal salts,[5] and BER- $Ni(OAc)_2$.[6] However, most of them have some disadvantages in relation to their general applicability, selectivity, ready availability, and operational convenience. Thus, a simple and efficient reducing agent of general applicability for the reduction of aryl nitro compounds will be well appreciated.

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Over the years, reducing agents and catalysts based on sulfur have had wide applications in organic chemistry because of their availability, easy handling, and low cost. Onopchenko et al.[7] have prepared cobalt polysulfide by treatment of cobaltous chloride with sulfur and have used it as a catalyst for the hydrogenation of aromatic nitro groups. In 1972, a report by Lalancete[8] outlined the preparation of sodium sulfurated borohydride, $NaBH_2S_3$ by treatment of $NaBH_4$ with a controlled amount of sulfur in anhydrous THF. The reduction of aromatic nitro compounds has been achieved with this reducing agent. Recently, Firouzabadi et al.[9] have prepared $Ca(BH_2S_3)_2$ as a modified and stable form of $NaBH_2S_3$ by metathetical reaction between $NaBH_2S_3$ and $CaCl_2$ in THF. They have reported the reduction of aryl nitro compounds with this modified reducing agent in dry THF.

Direct application of sulfur in the reduction of a nitro group was reported in 1950 by Hirao[10] who outlined the application of sulfur in dilute NaOH for the reduction of $PhNO_2$ according to the equation:

$$2\ PhNO_2 + 6\ S + 6\ NaOH \xrightarrow{H_2O} 2\ PhNH_2 + 3\ Na_2S_2O_3 + H_2O$$

The facile reduction of $NO_2$ by this method was however disturbed by further substitution in the aromatic ring.

Many interesting reactions under dry conditions in the presence of inorganic solids such as alumina,[11] clay,[12] and silica gel[13] have been reported in recent years. The notable advantages for most of these reactions are operational simplicity, generality, excellent regioselectivity, absence of side reactions, and quantitative yields.

Having the above facts in mind, we now report that a system comprising Alumina/$S_8$/NaOH is able to perform reduction of aryl nitro compounds conveniently under nonsolvent conditions.

## RESULTS AND DISCUSSION

Several reduction reactions of nitrobenzene were performed at various temperatures and with different amounts of sulfur, inorganic solid, and sodium hydroxide in order to find the most adequate condition for this reaction under solvent-free conditions. In a preliminary study, the effect of some inorganic solids on the yield of reduction was investigated with the reaction of nitrobenzene as a model reaction. As shown in Table I, alumina is the best solid support for this reaction. The required mole

**TABLE I** Reduction of Nitrobenzene with Sulfur and NaOH on Various Solid Supports at 80°C

| Support surfaces | Time (h) | Conversion |
|---|---|---|
| Alumia | 0.5 | 100 |
| Silica gel | 15 | 30 |
| $K_2CO_3$ | 24 | 5 |
| $Na_2SO_4$ | 2 | 50 |
| Clay | 24 | 20 |
| Molecular sive | 24 | 10 |

ratio, 3:3:1, of sulfur, NaOH, and substrate, respectively, alumina 2g, and the maximum oil bath temperature of 80°C were found to be optimal conditions.

$$\mathbf{Ar\text{-}NO_2} \xrightarrow[\text{Solvent free condition}]{\text{Alumina}/S_8/\text{KOH}} \mathbf{Ar\text{-}NH_2}$$

**SCHEME 1**

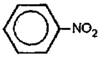
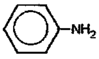
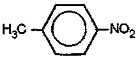
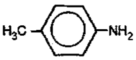
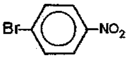
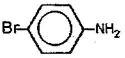
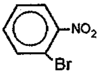
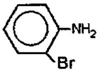
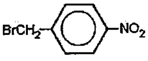
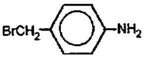
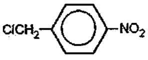
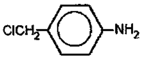
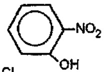
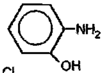
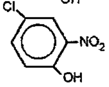
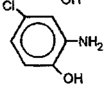
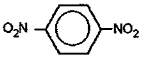
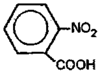
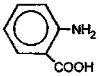
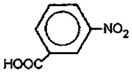
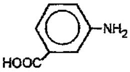
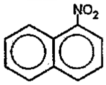
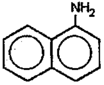
A variety of nitroarenes carrying electron-withdrawing or electron-donating groups are reduced in the presence of alumina/$S_8$/NaOH system to the corresponding primary amines as exclusive and virtually pure products according to TLC and $^1H$ NMR under solvent-free conditions in good isolated yields. Several examples illustrating this facile procedure for the reduction of nitroarenes are listed in Table II.

It is noteworthy that under similar reaction conditions, when nitro benzene was reacted with sulfur and NaOH in the absence of alumina, GC and TLC analysis of the reaction mixture did not show formation of any product after 24 h. By this method, absolute selectivity is observed for the reduction of nitro functionality in the presence of phenol, carboxylic acid, aldehyde, and benzyl halide groups (Table I).

## CONCLUSION

We believe that the present methodology offers a simple and efficient method for the reduction of aromatic nitro compounds. In addition, availability of the reagent, easy work-up, high yields, and absolute selectivity compares favorably with known methods and makes this method a useful addition to the present methodologies.

**TABLE II** Reduction of Aromatic Nitro Compounds with Alumina Supported Sulfur and NaOH

| Entry | Substrate | Product | Time | Yield (%)[a,b] |
|---|---|---|---|---|
| **1** |  |  | 0.5 | 86 |
| **2** |  |  | 0.5 | 67 |
| **3** |  |  | 5 | 81 |
| **4** |  |  | 2 | 80 |
| **5** |  |  | 2 | 77 |
| **6** |  |  | 2.5 | 83 |
| **7** |  |  | 4 | 68 |
| **8** |  |  | 3 | 69 |
| **9** |  |  | 1 | 85 |
| **10** |  |  | 7 | 65 |
| **11** |  |  | 4 | 73 |
| **12** |  |  | 0.7 | 64 |
| **13** |  |  | 1 | 68 |

[a] Yields referred to isolated yields.

[b] Products were characterized by comparison of their physical data, IR, NMR spectra with known samples.

# EXPERIMENTAL

## General

Products were characterized by comparison of their physical data with those of authentic samples. All yields refer to isolated products. IR spectra were recorded on a Shimadzo 450 spectrophotometer. $^1$H NMR spectra were recorded on a Bruker Avance DPX instrument (250 MHZ). Melting points were determined in open capillaries with a Galen-Kamp melting point apparatus. TLC accomplished the purity determination of the substrates and reaction monitoring on silica gel polygram SILG/UV 254 plates.

## General Procedure for the Reduction of Nitro Compounds

A mixture of nitroarene, sulfur, alumina, and sodium hydroxide was ground in a mortar and then placed in a round-bottomed flask and magnetically stirred and heated in an oil bath at 80°C for the appropriate time (see Table II). The reaction mixture was then allowed to reach room temperature and acidified with HCl solution (10%) until the pH of the reaction mixture reached 1. The reaction mixture was filtered and the solid material was washed with dichloromethane several times. The combined filtrate was extracted with dichlomethane (2 × 15 ml). The aqueous layer was separated and the pH of the mixture adjusted to about 11 with a solution of NaOH (10%). The aqueous layer was extracted again with $Et_2O$ (15 ml) and the combined extracts were dried over anhydrous $Na_2SO_4$ and evaporated to give the product in 64–86% isolated yields.

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