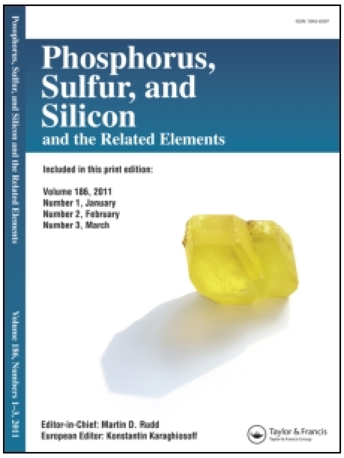

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FACILE REDUCTION OF AROMATIC NITRO COMPOUNDS WITH HYDROIODIC ACID UNDER MICROWAVE IRRADIATION ON SOLID SUPPORT

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Reduction of aromatic nitro compounds to amine with hydroiodic acid was revisited. Under microwave irradiation on solid support the reduction proceeded efficiently and rapidly.

Keywords: Aromatic nitro compounds; hydroiodic acid; microwave irradiation; reduction; solid support

Aromatic amines are used extensively as intermediates in the preparation of important industrial chemicals such as dyes and pharmaceutical and agricultural chemicals. They can be obtained simply by the reduction of aromatic nitro compounds using catalytic hydrogenation.[1] Several reducing agents have been used to reduce aromatic nitro compounds, with the most classical being zinc, tin, and iron.[2] Other reagents have been also used to accomplish this important chemical transformation.[3] However, relatively few reagents are known for the synthetically and industrially important reaction on solid support[4] and under microwave irradiation.[5]

The solvent-free application of supported reagents in combination with microwave irradiation provide ideal reaction conditions with special attributes such as selectivity and reactivity. Short reaction time, and easy work up procedures.[6]

In 1947 Bruce and Perez-Medina[7] reported that in refluxing hydroiodic acid a nitro group in the pyridine ring can be effeciently reduced

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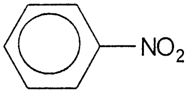
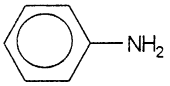
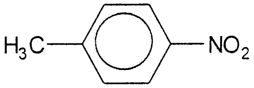
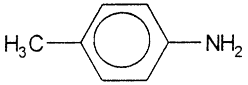
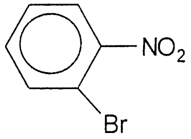
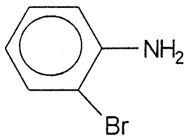
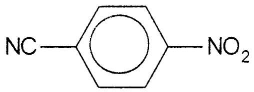
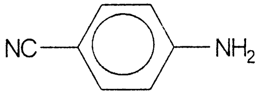
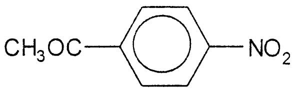
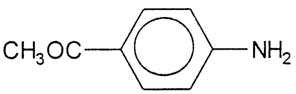
to aminopyridine. In 1971[8] some chemoselectivity was also observed in the Hl-mediated reduction of nitro aromatic compounds to aromatic amines. In 2001 simple and chemoselective reduction of aromatic nitro compounds to aromatic amines was revisited.[3d]

In continuation of our investigation on solvent-free reaction conditions under microwave irradiation,[9] herein we report our results for a solvent-free microwave-reduction protocol that leads to a facile preparation of aromatic amines from the corresponding nitro compounds with hydroiodic acid supported onto solid materials such as alumina and silica gel. Two series of experiments were performed to identify and optimize the best solid support material and the appropriate catalyst to affect the reduction of aromatic nitro compounds.

Among alumina, silica gel, clay, zeolite, and nontraditional solid support material such as NaCl, NaBr, Nal, KCl, KBr, Kl, Na_2SO_4, K_2SO_4, $CaCO_3$, etc., alumina gave the best results (Table I). In the second series of experiments, the optimized amount of hydroiodic acid was determined. The optimized condition is accomplished when for 1 mmol of aromatic nitro compound 1.5 mmol of 57% Hl supported on 2 g of alumina was used.

TABLE I Reduction of Aromatic Nitro Compounds with 57% HI Supported onto Solid Material Under Microwave Irradiation in Solventless System

Entry	Substrate	Reaction time (min)	Product	Yield (%)
1		6		94
2		5		93
3		6		95
4		4		97
5		4		96

The reaction is simply conducted by mixing 57% Hl with alumina using pestle and mortar. Grinding of an aromatic nitro compound with this mixture gives an intimate mixture upon which exposure to microwave irradiation affords the corresponding aromatic amine (Table I).

In summary, we have shown an expeditious, facile, and rapid method for the synthesis of aromatic amines by the reduction of aromatic nitro compounds via alumina supported hydroiodic acid under microwave irradiation in solventless system within a few minutes. Easy workup procedure and high yields are the other advantages of this method. Moreover, acid labile, nitrile, and reductable ketones did not undergo hydrolysis and reductions (entries 4 and 5 in Table I).

EXPERIMENTAL SECTION

All starting materials were commercially available. All products were known and identified by comparison of their physical and spectroscopic data with those of authentic samples. Yields refer to isolated product. Although we did not observe any accident, use of a microwave oven in an efficient hood is highly recommended.

Reduction of Aryl Nitro Compound: General Procedure

Alumina (2 g) was mixed with hydroiodic acid 57% (1.5 ml) using pestle and mortar. To this mixture in a beaker an aromatic nitro compound (1 mmol) was added and mixed thoroughly with a spatula. The beaker was placed in a household microwave oven for the specified time. The progress of reaction was monitored by TLC (petrol ether: ethyl acetate 8:2). Upon the completion of the reaction and after cooling to room temperature, ethyl acetate (5 ml) was added. The mixture was filtered. The dark purple solution was washed successively with a saturated aqueous solution of $Na_2S_2O_3$ (for the distortion of iodine formed) and brine. The colorless organic layer was dried over Na_2SO_4, filtered and evaporated to dryness. The crude residue was subjected to column chromatography using petroleum ether: ethyl acetate (8:2) as eluent to afford the corresponding aromatic amine (Table I):

$$\mathrm{ArNO_2} \xrightarrow[\text{MW}]{\text{57\% HI, solid support}} \mathrm{ArNH_2}$$

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