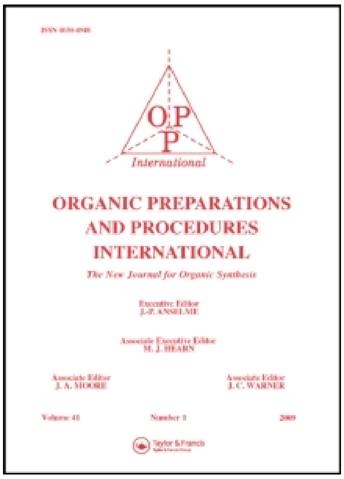

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SIMPLE, HIGH YIELD PREPARATION OF 3-NITRO-1,2-PHENYLENEDIAMINE

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SIMPLE, HIGH YIELD PREPARATION OF 3-NITRO-1,2-PHENYLENEDIAMINE

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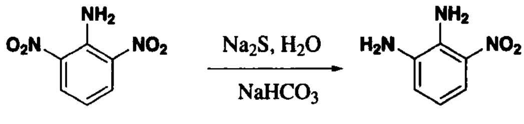
1,2-Phenylenediamines are often used in the synthesis of condensed heterocycles.[1] For example, 3-nitro-1,2-phenylenediamine (**2**) is a useful starting material for the synthesis nitroheterocycles such as 4(7)-nitrobenzimidazole,[2] 4-nitro-1-methylbenzimidazole,[3] 4(7)-nitro-2-methylbenzimidazole,[4] 4(7)-nitrobenzotriazole,[4] 5-nitroquinoxaline,[5] 5-nitro-2,3-dimethylquinoxaline[6] or 5-nitro-2,3-diphenylquinoxaline:[4]



1 **2**

Compared to 4-nitro-1,2-phenylenediamine, 3-nitro-1,2-phenylenediamine (**2**) is difficult to obtain. It was first prepared using partial reduction (Zinin reaction) of 2,6-dinitroaniline (**1**), itself prepared by a multi-step procedure.[7] Slow addition (1 h) of an aqueous solution of **1** to an aqueous solution of sodium sulfide and sodium bicarbonate at 60° gave a 70-80% yield of **2**[2] while addition of a methanolic solution of **1** to an aqueous solution of sodium sulfide and sodium bicarbonate preheated to 50°, followed by a 2-4 h reflux afforded **2** in 96% yield.[8] Other related procedures involve the use of hydrogen sulfide in ammonia and ethanol at reflux (no yield)[4] or ammonia hydrosulfide at reflux for 1 h (86%).[9] Transfer hydrogenation from cyclohexene or hydrazine with Pd/C or ruthenium on carbon in ethanol occurs readily in excellent yield (90-95%) in 10 min. or 3 h on a steam bath but the catalysts are expensive.[10,11] Recent methods exploit the ring opening of 4-nitro-2,1,3-benzoselenadiazoles with expensive hydroiodic acid in yields of 67% and 76%.[12,13]

All of these methods suffer from some disadvantages such as the use of organic solvents, expensive and/or difficult to handle reagents, low yields. We now describe a procedure which utilizes only water as solvent and simply handled and inexpensive reagents. The starting material must be pure and the temperature carefully monitored. The reaction may be scaled up to ten times the amount reported below.

EXPERIMENTAL SECTION

The melting point was determined on a Kofler micro hot-stage and is uncorrected. NMR spectra were recorded on a Varian VXR-300 NMR spectrometer in $CDCl_3$+DMSO-d_6 in 5 mm tubes at 299.9 MHz and 75.0 MHz for proton and carbon respectively relative to internal TMS.

3-Nitro-1,2-phenylenediamine (2).- A suspension of freshly recrystallized 2,6-dinitroaniline (from ethanol)[7] (10 g, 0.055 mol) in water (200 mL) was heated to 60° with stirring for about 10 min. To this suspension was then added a solution of sodium sulfide (14 g, anhydrous) and sodium bicarbonate (14 g) in water (300 mL). The reaction mixture was stirred at 70-75° for 1 hour and left to cool overnight. The separated deep red crystals were collected, washed with cold water (300 mL) and dried to yield 8.26 g (99%) of **2**. Recrystallisation from toluene (1 g/~ 15 mL) gave 5.8-6.6 g (70-80%) of product, mp. 161°, lit.[12] mp. 158-159°, lit.[2] mp. 159° as a red crystalline solid. ^{1}H NMR ($CDCl_3$+DMSO-d_6): δ 6.60 (t, 1H, H-5); 6.93 (d, 1H, H-6); 7.69 (d, 1H, H-4). ^{13}C NMR ($CDCl_3$+DMSO-d_6): δ 116.5 (C-6); 117.7 (C-4); 121.7 (C-5); 133.2 (C-2); 135.4 (C-3); 136.6 (C-1).

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