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> SHORT COMMUNICATIONS

Preparative Procedure for the Reduction of Substituted Nitroarenes with Hydrazine Hydrate in the Presence of a Nickel–Cobalt Nanocatalyst

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Abstract—A preparative procedure has been proposed for the reduction of substituted nitroarenes with hydrazine hydrate in the presence of a nanocatalyst based on cobalt–nickel nanoparticles, which ensured selective formation of the corresponding anilines in 78–80% yield in 20–45 min.

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Catalytic reduction of nitro compounds is a universal method for the preparation of amines, which is widely used in practical organic synthesis. However, most of the known procedures do not ensure desired chemoselectivity, especially in the reduction of polyfunctionalized compounds. Due to their unique physical and chemical properties determined by large specific surface area, nanocatalysts provide a promising alternative to homogeneous and heterogeneous catalysts [1]. We previously proposed a procedure for the reduction of aromatic nitro compounds over Raney nickel [2]. However, the reduction of functionalized and/or substituted aromatic nitro compounds with hydrazine hydrate in the presence of Raney nickel was accompanied by hydrogenation of C=N bond and (in some cases) aromatic heterocycle.

Herein, we propose a selective preparative procedure for the reduction of substituted nitroarenes with hydrazine hydrate in the presence of a cobalt–nickel nanosol. The reduction of nitrobenzenes is a multistep process which can either involve successive formation of nitrosobenzene and phenylhydroxylamine or follow a condensation path through azoxybenzene, azobenzene, and hydrazobenzene intermediates **A–C** [3].

Using a weakly active sample of nickel nanocatalyst, we isolated azobenzene **B** (according to the MS data) as by-product in addition to the target benzene-1,3-diamine, which indicated that the condensation path is operative.

The reduction of nitroarenes 1 and 2 with hydrazine hydrate over a cobalt–nickel nanocatalyst was complete in 20–45 min, and the corresponding phenylene-



[†] Deceased

diamines **3** and **4** were obtained in 78–80% yield. An important factor responsible for the catalytic activity of the Ni/Co composite is the ratio of initial nickel and cobalt nitrates. The most active was the nanocatalyst obtained from Ni(NO₃)₂·6H₂O–Co(NO₃)₂·6H₂O at a ratio of 5:1. The nanocatalyst can be readily separated from the products by filtration and reused.

Thus, the efficiency of the Ni/Co nanocatalyst in the reduction of nitroarenes with hydrazine hydrate is comparable with the efficiency of Raney nickel, and the proposed procedure conforms to the "green chemistry" principles.

Nickel–cobalt nanocatalyst. Aliquots of distilled water, 200 mmol of Ni(NO₃)₂ · $6H_2O$, and 200 mmol of Co(NO₃)₂ · $6H_2O$ were mixed together, three aliquots of NaBH₄ (458 µL each, 300 mmol) in DMSO were added in 1-min intervals with stirring on a magnetic stirrer, and the resulting sol was subjected to ultrasonic treatment for 2 h while gradually raising the temperature to 52–58°C. The concentrations of the components in the reaction mixture were as follows: DMSO, 15 vol %; Ni(NO₃)₂ · $6H_2O$, 15 mmol; Co(NO₃)₂ · $6H_2O$, 3 mmol; NaBH₄, 55 mmol; water–DMSO ratio 1:1. The Ni/Co sol was separated by centrifugation for 10 min at 10000 rpm, washed with distilled water and then with ethanol, and stored wet at ~ $6^{\circ}C$.

Reduction of nitroarenes 1 and 2 (general procedure). A suspension of 0.5 mmol of nitro compound 1 or 2 in 1 mL of ethanol was heated to 50°C, 0.05 mmol of Ni/Co nanocatalyst in 1 mL of ethanol was added with stirring, the mixture was stirred for 5–7 min, and 0.18 mL (3.5 mmol, 5 equiv) of hydrazine hydrate was added dropwise. The mixture was refluxed for 20– 45 min, the progress of the reaction being monitored by TLC. When the reaction was complete, the warm mixture was filtered through a layer of celite, the sorbent was washed with ethanol, and the filtrate was combined with the washings and evaporated. The residue was dissolved in 10 mL of ethyl acetate, the solution was washed with water and evaporated to 1/3 of the initial volume, and the product was precipitated with petroleum ether. In the isolation of compound 3, the filtrate was acidified with 0.4 mL of concentrated aqueous HCl to pH 1, and the precipitate of 4-methylbenzene-1,3-diamine dihydrochloride was filtered off, washed with dilute (1:1) aqueous HCl, dried, and recrystallized from methanol-hexane.

4-Methylbenzene-1,3-diamine dihydrochloride (3). Yield 82%, white crystals, mp >200°C (decomp.). IR spectrum (KBr), v, cm⁻¹: 3300, 2980 (NH), 1612, 1580, 1475, 1200, 1190. Mass spectrum, m/z (I_{rel} , %): 122.05 (100), 108.02 (52) [M – CH₃]⁺, 78.01 (26), 51 (15). Found, %: C 43.00; H 6.22; Cl 36.37; N 14.35. C₇H₁₂Cl₂N₂. Calculated, %: C 43.10; H 6.20; Cl 36.35; N 14.36.

6-Methyl- N^1 -[**4-(pyridin-3-yl)pyrimidin-2-yl]benzene-1,3-diamine (4).** Yield 77%, yellow crystals, mp 138–140°C; published data [4]: mp 134–136°C. IR spectrum (KBr), v, cm⁻¹: 3340, 3235, 3044, 1580, 1551, 1450. Mass spectrum, m/z (I_{rel} , %): 277 (100) $[M]^+$, 262 (90) $[M - CH_3]^+$, 121 (20), 77 (4.5).

The IR spectra were recorded in KBr on a Bruker Tenzor 27 spectrometer. The mass spectra were obtained on a Thermo Scientific Trace GC Ultra DSQ II instrument. The elemental compositions were determined on a Vario MICRO Cube automated CHNS analyzer. The melting points were measured on a Kofler hot stage. Ultrasonic treatment was performed with an ElmaSonic S30H ultrasonic bath (Germany).

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