

Note

Reduction of aromatic nitro compounds using microwave heating assisted with alumina-supported hydrazine / $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

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An easy, rapid, convenient method for the reduction of aromatic nitro compounds is developed by using microwave heating assisted with alumina-supported hydrazine/ $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Keywords: Aromatic nitro compounds, microwave heating, alumina-supported hydrazine

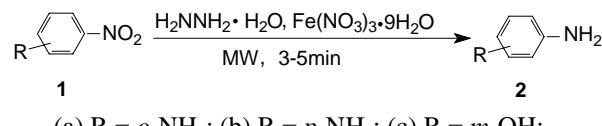
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Aromatic amines are widely used as intermediate for dyes, photographic materials, pharmaceutical and agricultural chemicals and as antioxidants. They are generally prepared by reduction of aromatic nitro compounds. Because of its significance in organic chemistry, the development of new reductants and methods for the reduction of aromatic nitro compounds is to receive continuous attentions.

Hydrazine hydrate has been extensively used for the reduction of aromatic compounds in the presence of heterogeneous catalysts such as activated zinc-copper¹, Zn-C², Fe-C³, Pd-C⁴⁻⁶, Pt-C⁴⁻⁵, RaneyNi^{5,7-9}, $\text{FeCl}_3 \cdot 9\text{H}_2\text{O}$ -activated carbon¹⁰⁻¹³, Fe(III) oxides¹⁴⁻¹⁶, Fe(III)-MgO¹⁷, graphite¹⁸ and clays¹⁹. The reaction is usually conducted in refluxing alcoholic solvent or dioxane that requires several hours. Consequently, easy, rapid, convenient methods for the reduction of aromatic nitro compounds are required.

Microwave irradiation has been successfully applied in organic synthesis. Recently reaction facilitated by microwaves under solvent-free condition have attracted more attention because of their enhanced selectivity, reducing reaction time, easier work-up procedure²⁰. Recyclability of the inorganic solid support is often

possible thus rendering the procedure relatively environmentally acceptable. It was tried to use alumina-supported hydrazine / $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to reduce aromatic nitro compounds and demonstrated that the reaction proceeded smoothly (**Scheme I**). Compared with the conventional solution phase reactions, the merits are reduced reaction time, easier work-up procedure, and milder reaction conditions (**Scheme I**). The results are summarized in **Table I**.



(a) R = *o*-NH₂; (b) R = *p*-NH₂; (c) R = *m*-OH;
(d) R = *o*-OH; (e) R = *p*-OH; (f) R = *p*-Cl;
(g) R = *p*-CH₃; (h) R = *p*-OCH₃

Scheme I

Experimental Section

Melting points were determined on a Kofler micro melting point apparatus without correction. IR spectra were recorded on a FTS-40 spectrophotometer in KBr. ¹H NMR spectra were measured with a mercury 300 or a Bruker DPX-400 instrument for CDCl₃ solvent using TMS as internal standard.

General Procedure. Aromatic nitro compound (1 mmole), alumina (1.0 g) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.3 mmole) were mixed thoroughly in an agate mortar. The mixture was placed in a big tub, having diameter of 2 centimeter. Then added hydrazine hydrate (4 mmole) to the mixture. The tub was placed in a Galanz Cambi-Grill microwave oven (750 w) at minimal power level for 3-5 minutes, the progress of the reaction was monitored by TLC using acetone-petroleum (1:2.5) as the eluent. Upon completion of the reaction, the contents were cooled to room temperature and the product was extracted with ethanol or ethyl ether (2×10 mL). The product was filtered over alumina and the solvent was removed under reduced pressure. The pure products thus obtained were further purified by recrystallization from ethanol.

Compound 2a: IR (KBr): 3392, 3297, 3193, 1630, 1590, 1500 cm⁻¹; ¹H NMR (CDCl₃): δ 3.28 (s, 4H, NH₂), 6.67 (m, 4H, Ar-H).

Table I—Microwave-assisted reduction of aromatic nitro compounds (**2a-2h**) with alumina-supported hydrazine hydrate and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

Product no.	Yield (%)	m.p. $^{\circ}\text{C}$	Lit m.p. $^{\circ}\text{C}$
2a	85	98-00	102-04 (ref 21)
2b	97	142-44	145-47 (ref 21)
2c	53	120-22	123 (ref 21)
2d	93	168-70	172-74 (ref 21)
2e	87	186-88	188-90 (ref 21)
2f	70	69-71	71-72 (ref 21)
2g	65	41-43	44-45 (ref 21)
2h	53	54-56	56-58 (ref 21)

Compound 2b: IR (KBr): 3375, 3300, 3200, 1650, 1525 cm^{-1} ; ^1H NMR (CDCl_3): δ 4.00 (s, 4H, NH_2), 6.39 (s, 4H, Ar-H).

Compound 2c: IR (KBr): 3370, 3300, 3040, 1600, 1510, 1470 cm^{-1} ; ^1H NMR (CDCl_3): δ 4.71 (s, 2H, NH_2), 6.06-6.78 (m, 4H, Ar-H), 8.78 (s, 1H, OH).

Compound 2d: IR (KBr): 3370, 3300, 3050, 1600, 1510, 1470 cm^{-1} ; ^1H NMR (CDCl_3): δ 6.92-7.53 (m, 4H, Ar-H), 8.62 (m, 3H, NH_2 , OH)

Compound 2e: IR (KBr): 3330, 3280, 3020, 1610, 1505, 1470 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.12-7.45 (m, 4H, Ar-H), 8.70 (s, 3H, NH_2 , OH).

Compound 2f: IR (KBr): 3480, 3400, 1620, 1500 cm^{-1} ; ^1H NMR (CDCl_3): δ 5.03 (s, 2H, NH_2), 6.60-7.02 (m, 4H, Ar-H).

Compound 2g: IR (KBr): 3430, 3350, 3220, 2920, 2760, 1630, 1515 cm^{-1} ; ^1H NMR (CDCl_3): δ 2.18 (s, 3H, CH_3), 3.25 (s, 2H, NH_2), 6.33-6.79 (m, 4H, Ar-H).

Compound 2h: IR (KBr): 3420, 3350, 3050, 2830, 2740, 1630, 1510 cm^{-1} ; ^1H NMR (CDCl_3): δ 3.38 (s, 2H, NH_2), 3.73 (s, 3H, CH_3), 6.68-6.72 (m, 4H, Ar-H).

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