

## Reduction of Aromatic Nitro Compounds under Solvent-free Conditions using Alumina-supported Hydrazine/ $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

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Aromatic nitro compounds were easily reduced to the corresponding amino compounds with hydrazine hydrate supported on alumina in the presence of  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

**Keywords:** Reduction; Hydrazine hydrate; Aromatic nitro compounds; Amino compounds; Microwave heating;  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ .

### INTRODUCTION

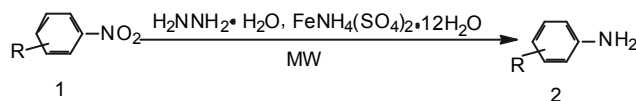
Aromatic amines are widely used as intermediates for dyes, photographic materials, pharmaceutical and agricultural chemicals, and as antioxidants. Hence, particular interest has been directed toward the synthesis of these compounds. Reduction of aromatic nitro compounds is one of the important routes to prepare them. It has been reported that an ecofriendly alternative to the commonly used reduction methods effected by means of iron and acid or sulphides is the use of hydrazine hydrate as hydrogen donor in the presence of heterogeneous catalysts such as activated zinc-copper,<sup>1</sup> Zn-C,<sup>2</sup> Fe-C,<sup>3</sup> Pd-C,<sup>4-6</sup> Pt-C,<sup>4-5</sup> RaneyNi,<sup>5,7-9</sup>  $\text{FeCl}_3 \cdot 9\text{H}_2\text{O}$ -activated carbon,<sup>10-13</sup> Fe(III) oxides,<sup>14-16</sup> Fe(III)-MgO,<sup>17</sup> graphite<sup>18</sup> and clays.<sup>19</sup> However, most of the processes mentioned above have one or more drawbacks, such as long reaction time, relatively expensive catalysts, and a tedious work-up. Consequently, easy, rapid, convenient methods for the reduction of aromatic nitro compounds are required.

### RESULTS AND DISCUSSION

Microwave irradiation has been successfully applied in organic synthesis. Recently, reactions facilitated by microwaves under solvent-free conditions have attracted more attention because of their enhanced selectivity and milder reaction conditions. Recyclability of the inorganic solid support is often possible thus rendering the procedure relatively environmentally acceptable. In this way, we successfully reduced the aromatic nitro compounds with hydrazine hydrate sup-

ported on alumina in the presence of  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ . All the products were characterized by comparison of their TLC, IR spectra and melting or boiling points with authentic samples. The results of the reduction are summarized in Table 1.

### Scheme I



- (a) R = *o*-NH<sub>2</sub>; (b) R = *p*-NH<sub>2</sub>; (c) R = *m*-OH;  
 (d) R = *o*-OH; (e) R = *m*-OCH<sub>3</sub>; (f) R = *p*-Cl;  
 (g) R = *p*-CH<sub>3</sub>; (h) R = *p*-OCH<sub>3</sub>

Hydrazine hydrate, known as an excellent reductant, has been employed in many reactions. It has been reported that with some catalysts (such as  $\text{Cu}^{2+}$ ),<sup>20</sup> reduction of symmetrical multiple bonds proceeded readily, whereas reaction of more polar functions were rather difficult. The methods mentioned above illuminated that hydrazine hydrate is a good reductant for aromatic nitro compounds. Further work is in progress to understand the mechanism of the reactions over these catalysts.

### EXPERIMENTAL

Aromatic nitro compound (1 mmol), alumina (1.5 g) and  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$  (1.2 g) were mixed thoroughly in

Table 1. Microwave-assisted Reduction of Aromatic Nitro Compounds with Alumina-supported Hydrazine Hydrate and Catalytic  $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ 

Product	Reaction time (min)	Yield (%)	M.P./B.P (°C)	Lit M.P./B.P (°C)
2a	3	83%	98-100	102-104 <sup>21</sup>
2b	3	93%	142-144	145-147 <sup>21</sup>
2c	5	65%	120-122	123 <sup>21</sup>
2d	3	83%	168-170	172-174 <sup>21</sup>
2e	4	65%	246-248 (B.P)	251 <sup>21</sup> (B.P)
2f	3	50%	69-71	71-72 <sup>21</sup>
2g	4	50%	41-43	44-45 <sup>21</sup>
2h	3	60%	54-56	56-58 <sup>21</sup>

an aggregate of tar. The mixture was placed in a big tub. Then hydrazine hydrate (2 mL) was added to the mixture. The tub was placed in a Galanz Cambi-Grill microwave oven (750W) at minimal power level for a specified time; the progress of the reaction was monitored by TLC. On completion of the reaction, the contents were cooled to room temperature and the product extracted into ethanol or ether (2 × 10 mL). The alumina was filtered and the solvent was removed under reduced pressure to afford the product that was further purified by recrystallization from ethanol.

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