

Organic Sonochemistry. Ultrasonic Acceleration of the Reduction of Aromatic Nitro Compounds with Hydrazine-Iron in the Presence of Activated Carbon

Byung Hee Han¹, Dae Hyun Shin and Sung Yun Cho

The Department of Chemistry, College of Science Chungnam National University, Daejeon 300-31, Korea
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Hydrazine has been used to reduce aromatic nitro group in the presence of Pd-C, Pt-C, Raney Ni¹ or FeCl₃·6H₂O-C². However, it is unfortunate that methods were required relatively high temperature and longer reaction time.^{1,2} Consequently, side products such as azo compounds and hydroxyamines, were often accompanied and resulted in the separation problems. Recently, we reported that hydrazine-palladium couple was a very good hydrogenation reagent to olefins under sonic irradiation.³ In a development of sonic reduction reactions, we have found that aromatic nitro compounds are easily reduced to aromatic amino compounds using hydrazine hydrate, iron powder, activated carbon and sonic waves (50KHz). Our results are summarized in the Table.

In a typical experiment, 10 mmol of an aromatic nitro compound, 1.8 mmol of iron powder (10%C) and 20 mmol of hydrazine hydrate were added to 5 ml of absolute ethanol. The reaction mixture, contained in a 100 ml round bottom flask which was partly submerged in a common ultrasound laboratory cleaner (117V, 150W, 50KHz, 50/60Hz). A strong cavitation

dispersed a reaction mixture immediately and gases (presumably N₂ and H₂) were evolved. Reactions were run under a nitrogen atmosphere and bath temperature was maintained at 25°C by cooling coil. The work up procedure was very simple. The contents were filtered and washed with ethanol or benzene. The solvents were removed by flash evaporation. The products were characterized by comparison of their physical and chemical properties with those of authentic sample. The reduction never goes to completion without sonication. For example, in case of nitrobenzene, when 4 times large excesses of iron and hydrazine hydrate were used, only 40% yield of aniline was obtained after overnight with simply stirring at room temperature. Heating to reflux gave impure aniline. In the absence of activated carbon, reaction did not occur at all even under sonic irradiation. Iron-hydrazine couple reduced selectively to only aromatic nitro group not aliphatic nitro group. When we applied this reducing reagents to nitroethane, 100% of nitroethane was recovered after usual work up even with 4 times excesses of iron-hydrazine hydrate under 2 hour sonication. As indicated, high yields and mild conditions are advantage over the previous methods. Also, ordinary iron powder is directly usable. Work is now in progress to broaden the scope of the reducing system to other substrates.

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TABLE: Ultrasound Accelerated Reduction of Aromatic Nitro Compounds to Amino Compounds with NH₂NH₂·H₂O-Fe(10%C) in Ethanol*

Nitro Compound	Amino Compound	Yield (%, isolated)
C ₆ H ₅ -NO ₂	C ₆ H ₅ -NH ₂	95
<i>p</i> -CH ₃ C ₆ H ₄ -NO ₂	<i>p</i> -CH ₃ C ₆ H ₄ -NH ₂	90
<i>p</i> -NH ₂ C ₆ H ₄ -NO ₂	<i>p</i> -NH ₂ C ₆ H ₄ -NH ₂	95
<i>o</i> -CH ₃ OC ₆ H ₄ -NO ₂	<i>o</i> -CH ₃ OC ₆ H ₄ -NH ₂	90
<i>p</i> -CH ₃ OC ₆ H ₄ -NO ₂	<i>p</i> -CH ₃ OC ₆ H ₄ -NH ₂	88
1-Nitronaphthalene	1-Aminonaphthalene	92
4-Nitrodiphenylether	4-Aminodiphenylether	89

*Iron powder(325 mesh) was used. All of our reactions were run at room temperature and worked up after one hour.

References

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- (2) T. Hirashima and O. Manabe, *Chem. Lett.*, 259 (1975).
- (3) D. H. Shin and B. H. Han, *Bull. Kor. Chem. Soc.*, **6**(4), 247 (1985).