

유기초음파 화학. 초음파를 이용한 방향족 및 지방족 니트로 화합물의 환원반응

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Organic Sonochemistry, Ultrasonic Acceleration on the Reduction of Aromatic and Aliphatic Nitro Compounds with Palladium-Hydrogen

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The rapid and selective reduction of nitro compounds is still an important synthetic area,¹ particularly when a molecule has several other reducible groups.

Nitroaliphatic compounds can be reduced by high pressure hydrogenation^{2,3}, LiAlH_4 ^{4,5}, Al-Hg ⁶⁻⁹, NaBH_4 -Pd/C¹⁰, NaHTe ¹¹, NH_2NH_2 -Pd/C¹², HCOONH_4 -Pd/C¹³, and NaBH_4 NiCl₂¹⁴. These are also applicable reagents to the reduction of aromatic nitro compounds. While nitroarenes can be reduced to the corresponding amino compounds by Fe(Sn)-HCl ¹⁵, Pd/C, Pt/C, Raney Ni-NH₂NH₂¹⁶, NaBH_4 ¹⁷, Fe¹⁸, Rh¹⁹, Ru²⁰, PtCl₂-CO²¹, NH_2NH_2 -Graphite²², NaBH_4 -Co²³, Na_2S ²⁴, activated Zn-NH₂NH₂²⁵, Pd-HCOOH²⁶ and FeCl_3 -NH₂NH₂²⁷.

The methodology described by the authors is inappropriate due to the necessity of preparing of catalysts, to longer reaction times, or to the relatively high pressure and temperature required.^{2,3}

We have therefore taken a sonochemical approach²⁸⁻³¹ to solve this problem. Previously, we reported that the sonic irradiation with an ultrasonic laboratory cleaner enhances significantly the

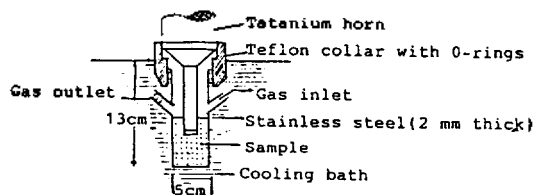


Fig. 1. Ultrasound experimental set-up.

rate of reduction for the aromatic nitro compounds with iron and hydrazine in the presence of activated carbon.³²

We have continued our studies and found that the reduction of aromatic and aliphatic nitro compounds under sonic irradiation with a probe is essentially quantitative, giving the corresponding amino products in high yields without effecting other functional groups. The reduction using palladium and hydrogen (14 psi) under ultrasonic irradiation with a probe (Fig. 1) takes place smoothly within 1 hr at 0 °C. Our results are summarized in Table 1.

In a typical experiment, a dry nitrogen filled probe reactor was charged with 0.01 mol of aromatic nitro compound, 5% of palladium on carbon (0.2g, 9.39×10^{-5} mol), 20 ml of absolute ethanol

Table 1. Ultrasound accelerated reduction of aromatic and aliphatic nitro compounds^{a,b}

Nitro compound	Product	Yield(%) (isolated)	Comparison ^c (stirring, %, GC yield)
C ₆ H ₅ -NO ₂	C ₆ H ₅ -NH ₂	89	3
<i>o,m,p</i> -CH ₃ C ₆ H ₄ -NO ₂	<i>o,m,p</i> -CH ₃ C ₆ H ₄ -NH ₂	90,90,92	5(<i>para</i>)
<i>o,p</i> -CH ₃ OC ₆ H ₄ -NO ₂	<i>o,p</i> -CH ₃ OC ₆ H ₄ -NH ₂	93,90	
<i>o,p</i> -HOC ₆ H ₄ -NO ₂	<i>o,p</i> -HOC ₆ H ₄ -NH ₂	85,88	0,0
<i>m,p</i> -O ₂ NC ₆ H ₄ CHO	<i>m,p</i> -H ₂ NC ₆ H ₄ CHO	90,95	0,0
<i>o,p</i> -HOCH ₂ C ₆ H ₄ -NO ₂	<i>o,p</i> -HOCH ₂ C ₆ H ₄ -NH ₂	95,97	
<i>o,p</i> -ClCH ₂ C ₆ H ₄ -NO ₂	<i>o,p</i> -ClCH ₂ C ₆ H ₄ -NH ₂	88,87	1.5(<i>para</i>)
<i>m,p</i> -CH ₃ COC ₆ H ₄ -NO ₂	<i>m,p</i> -CH ₃ COC ₆ H ₄ -NH ₂	90,90	0,0
<i>o,m</i> -HOCC ₆ H ₄ -NO ₂	<i>o,m</i> -HOCC ₆ H ₄ -NH ₂	85.83	
<i>o</i> -ClC ₆ H ₄ -NO ₂	<i>o</i> -ClC ₆ H ₄ -NH ₂	86	7(68) ^d
	C ₆ H ₅ -NH ₂	14	3(32) ^d
<i>p</i> -O ₂ N-C ₆ H ₄ C≡N	<i>p</i> -H ₂ N-C ₆ H ₄ C≡N	89	
1-Nitronaphthalene	1-Aminonaphthalene	96	2
6-Nitroquinoline	6-Aminoquinoline	92	0
8-Nitroquinoline	8-Aminoquinoline	91	0
1-Nitropropane	1-Aminopropane	73 ^e	
1-Nitrobutane	1-Aminobutane	80 ^e	
Nitrocyclohexane	Aminocyclohexane	83 ^e	0

^aAll reactions were run at 0 °C in 20 ml of absolute ethanol and 25 ml of benzene using a 0.01 mol of the corresponding nitro compound and 9.39 × 10⁻⁵ mol of palladium (0.2g, 5% Pd on carbon) under hydrogen pressure (14 psi). ^bAll reactions were sampled after 1 hr, found to be complete by GC and worked-up. ^cWithout sonication. ^d24 hr stirring instead of 1 hr. ^eIsolated as its HCl salts.

and 25 ml of benzene. The ultrasonic probe was placed 1 cm below the reaction mixture. The reactor was cooled with an ice-water bath and then connected with hydrogen after being flushed with hydrogen.

After sonication for 1 hr, the probe with and gas connecting line were removed. The content was filtered and washed with ethanol and benzene. Removal of solvents by flash evaporation gave the corresponding amino compounds. The reaction products exhibited physical and spectral characteristics in accord with those of authentic samples.

The reduction of aliphatic nitro compounds was also examined and we found that nitroalkanes were readily reduced to aminoalkanes in 73-83% yields under the same conditions except for the longer ultrasonic irradiation time (2 hr). Product isolation was straightforward. The catalyst was

removed by filtration and the products were isolated as its hydrochloride adducts.

Milder conditions with high yields of selectively reduced amino products are the obvious advantages over conventional methods. Furthermore, direct sonication³² in the reaction solution and elimination of the difficulty in locating the sweet spot are an additional benefit compared to sonic irradiation with a bath type sonicator. The results indicate that application of this technique to other transformations of functional groups may result in the discovery of many three phase heterogeneous catalytic reactions and of syntheses metal carbonyls and methatheses.

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