

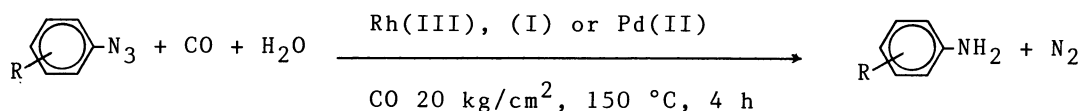
Transition Metal Catalyzed Reduction of Azidoarenes to
Aminoarenes with Carbon Monoxide-Water System

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Azidoarenes were readily transformed to aminoarenes in good yields under mild conditions with carbon monoxide and water in the presence of a catalytic amount of rhodium(III) complex, which is more catalytically active than rhodium(I) or palladium(II) complexes.

Transition metal catalyzed homogeneous water gas shift reaction (WGSR) is of current interest.¹⁾ The application of WGSR to the reduction of organic compounds have been widely attempted. One of the reactions is the reaction of azidoarenes to the corresponding aminoarenes.²⁾ In general, metal hydride species are well known to be key intermediates in such catalytic reactions as hydrogenation and hydrocarbonylation. These species were postulated to include a nucleophilic attack of water on a metal-coordinated carbonyl.³⁾ Our previous communication has indicated that a hydridocarbonyliron-carbon monoxide-moist ethanol system can be employed for reductive amination of azido compounds.⁴⁾

We herein wish to report the rhodium or palladium complex catalyzed reduction of azidoarenes to aminoarenes with carbon monoxide and water under mild conditions as follows :



In the general procedure, a mixture of rhodium(III) trichloride ($\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$) (4.3×10^{-2} mmol), an azidoarene (40 mmol), benzene (20 ml), and water (1.5 ml) was stirred at 150 °C under pressures of carbon monoxide (initial pressure, 20 kg/cm²) for 4 h in a 100 ml stainless autoclave.

Aniline was obtained in 61% yield under 20 kg/cm² of carbon monoxide pressure at 150 °C (Exp. 1). The yields decrease at lower temperature, 100 °C under even 30 kg/cm² of carbon monoxide pressure; aniline was obtained in 40% yield (Exp. 2). Under the same conditions, aniline was obtained in 44% yield using Pd(II)Cl₂ as a catalyst (Exp. 3). This catalyst appears to be less active than Rh(III)Cl₃·3H₂O for the azidoarenes.

Some representative results are listed in Table 1.

Table 1. Amination of Organic Azides using Rh or Pd Complex^{a)}

Exp. No.	Organic Azide (R-N ₃)	Product	Catalyst ^{b)}	Yield/% ^{c)}
1	Phenyl-	Aniline	A	61
2	Phenyl-	Aniline	A	40
3	Phenyl-	Aniline	B	44
4	Phenyl-	Aniline	C	34
5	p-Tolyl-	p-Toluidine	A	66
6	m-Tolyl-	m-Toluidine	A	70
7	o-Chlorophenyl-	o-Chloroaniline	A	64
8	o-Nitrophenyl-	o-Nitroaniline	A	26
9 ^{e)}	Benzyl-	- -	A	--
10	Benzyl-	- -	B	--

a) Benzene; 20 ml, CO; 20 atm., H₂O; 1.5 ml, Catalyst; 4.3 x 10⁻² mmol, 150°C 4 h.

b) Catalyst; A; RhCl₃ · 3H₂O, B; PdCl₂, C; [RhCl(NBD)]₂.

c) Based on the azidoarene used. Isolated yield.

d) 100 °C, 30 kg/cm².

e) 150 °C, 50 kg/cm², H₂O; 1.5 ml or 3.0 ml.

Para-, meta-, and ortho-substituted azidoarenes gave the corresponding aminoarenes in good yields without appreciable steric hindrance of their substituents (Exp. 5, 6, and 7). Some other important features of this reaction are indicated by the result using o-nitrophenyl azide as a substrate. Thus the reaction with RhCl₃ · 3H₂O gave o-nitroaniline in moderate yield accompanied with benzofurazane oxide⁵⁾ suggesting intramolecular cyclization of intermediate o-nitrophenyl nitrene. It turned out that the Rh(III), Rh(I), and Pd(II) complexes failed to aminate benzyl azide in various conditions probably due to the fact that the nitrene intermediate is unstable.

From these results we can conclude that our method using WGS condition is suitable for the reductive amination of azidoarene derivatives, but not suitable for that of alkylazides.

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