Tetrahedron Letters No. 37, pp.3385 - 3388, 1971. Pergamon Press. Printed in Great Britain.

RHODIUM CATALYZED REDUCTION OF NITRO COMPOUNDS TO AMINES WITH WATER AND CARBON MONOXIDE

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(Received in UK 23 July 1971; accepted in UK for publication 4 August 1971)

The reduction of nitro aromatics by carbon monoxide to the corresponding azo[1] and isocyanate[2-4] derivatives is well known. Group VIII metals are used as catalysts, mostly in combination with a Lewis acid, or a group V or VI element. Such methods either give poor yields or require drastic conditions.

We wish to report now a direct synthesis of aromatic amines by homogeneous catalytic reduction of the corresponding nitro derivatives with water under moderate carbon monoxide pressures*. The reaction, bearing the following over-all stoichiometry, proceeds practically quantitatively.

$$RNO_2 + 3CO + H_2O \xrightarrow[\text{Catalyst}]{} RNH_2 + 3CO_2$$

$R = \text{aryl}$

The catalyst preferably comprises a rhodium carbonyl derivative in aqueous organic bases[6].

The reaction is carried out in a stainless steel rocking autoclave. The resulting amines are separated by fractional distillation, analyzed and identified by gas chromatography, IR and NMR spectroscopy.

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* Since completion of the work reported here a patent[5] has appeared, which claims the reduction of aromatic nitro compounds to primary amines using hydrogen or carbon monoxide and water (or aliphatic alcohols) in the presence of catalysts consisting of at least two heavy metal oxides, hydroxides, or carbonates.

Some of the results obtained in the reduction of nitrobenzene have been compiled below in Table 1.

Table 1: Catalytic reduction of nitrobenzene with water and carbon monoxide[a]

Catalyst	Solvent	Temp. (°C)	CO-Pressure (atm)[b]	Yield of Amine [%] (based on nitro compd.)
Rh_2O_3	Pyridine	150	120	95
Rh_2O_3	Methanol	150	120	24
Rh_2O_3	Methanol[c]	150	120	4
$Rh_6(CO)_{16}$	Pyridine	55	50	4
$Rh_6(CO)_{16}$	N-MP[d]	50	50	85[e]
$[Rh(CO)_2Cl]_2$	Pyridine	150	120	92
$RhCl_3 \cdot 3H_2O$	Pyridine	150	120	90

[a] Constant reaction conditions: 0.1 mole nitro compound; 10^{-4} mole catalyst; 50-60 ml solvent; 3.5 hours; 0.5 l stainless steel autoclave.

[b] Initial pressure at room temperature. [c] No water used in this experiment.

[d] N-MP = N-methylpyrrolidine. [e] Yield after 12 hours.

Substantially milder conditions than hitherto cited in literature selectively furnish excellent amine yields. Subsequent carbonylation to formamide or urea derivatives does not take place. Any commonly available rhodium compound may serve as catalyst; the oxidation state of the metal plays no significant role. However, more rigorous conditions (150°C/120 atm CO) need to be applied with oxides or partially carbonylated salts of rhodium. With pre-formed rhodium carbonyls (e.g., $Rh_6(CO)_{16}$), the reaction proceeds smoothly even at 50°C and 50 atm. It is noteworthy in this context that, below 150°C no hydrogenation of nitrobenzene by $Rh_4(CO)_{12}$ is observed under normal hydroformylation conditions[4].

Water and an organic base as solvent are found indispensable for high conversions to amine. This seems to suggest a hydridorhodiumcarbonyl species[7] to be the active catalyst, whose preferred formation in aqueous organic bases may be analogous to that of ironcarbonyl-hydrides[8].

In the absence of water, no amine is formed, and the starting material is won back quantitatively. Replacement of water by other protic solvents, such as aliphatic alcohols, affords only poor yields of amine; no carbanilic acid ester is formed under these conditions. One can thus rule out an intermediacy of phenylisocyanate in the afore-mentioned reduction of nitro aromatics with water and carbon monoxide.

The basicity and nucleophilicity of the tertiary amine also play an important role in the synthesis. Particularly at lower temperatures, strongly basic solvents (e.g., N-methylpyrrolidine) prove to be more favourable than weak bases (e.g., pyridine). Further effective solvents include trimethylamine, triethylamine, N-methylpiperidine, dimethylformamide etc. Nitrotoluenes, dinitrobenzenes, nitroanilines, chloronitrobenzenes, and aromatic nitrosulphonic acids have also been successfully reduced to the corresponding amines.

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