

THE PLATINUM CATALYZED REDUCTION OF NITROARENES TO AMINOARENES  
WITH CARBON MONOXIDE AND WATER

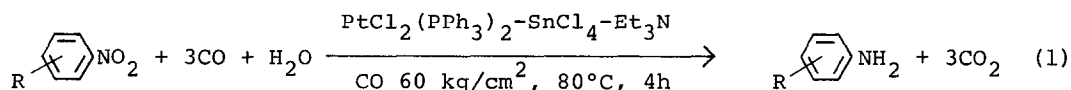
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Nitroarenes were readily transformed to aminoarenes in excellent yields under mild conditions with carbon monoxide and water in the presence of a platinum catalyst. Triethylamine,  $\text{SnCl}_4$  and  $\text{PPh}_3$  are essential for the high catalytic activity. Nitroarenes are reduced chemoselectively by this procedure.

Transition metal catalyzed homogeneous water gas shift reaction (WGSR) is of current interest. The applications of WGSR to the reduction of organic compounds have been widely attempted. One of these studies is the reduction of nitroarenes to the corresponding aminoarenes. In the reactions iron<sup>1)</sup>, rhodium<sup>2)</sup> and ruthenium<sup>3)</sup> clusters have been mostly used as effective catalysts.

We now wish to report the platinum complex catalyzed reduction of nitroarenes with carbon monoxide and water under mild conditions (eq.(1)).



In this reaction nitrobenzene is almost quantitatively reduced to aniline at 80°C using 0.5 mol% of  $\text{PtCl}_2(\text{PPh}_3)_2$  (Run 1).

The presence of triethylamine,  $\text{SnCl}_4$  and  $\text{PPh}_3$  is essential for the high activity of the platinum catalyst (Runs 1-4). It is noteworthy that nitroarenes are converted to aminoarenes with such a small amount of  $\text{Et}_3\text{N}$  and water. Tin(IV) chloride is the most effective, whereas  $\text{SnCl}_2$ ,  $\text{ZnCl}_2$ ,  $\text{FeCl}_3$  and  $\text{AlCl}_3$  in place of  $\text{SnCl}_4$  were less favorable.

The yield of aniline decreased at lower temperatures; 50 and 20°C (Runs 5,6). Under even 30  $\text{kg/cm}^2$  of carbon monoxide pressure aniline was obtained in 90% yield (Run 7), but in 54% yield under 15  $\text{kg/cm}^2$  (Run 8). This catalyst system appears to be widely active for the nitroarenes (Runs 9-10).

Hydrogen was not detected in gas phase after the reaction. Furthermore,

Table The Pt-catalyzed reduction of nitroarenes by use of CO-H<sub>2</sub>O a)

Run	Nitroarene R=	CO pres. /kg/cm <sup>2</sup>	Temp /°C	Conv. b) /%	Yield of b) aminoarene /%
1	H	60	80	100	97
2 c)	H	60	80	75	74
3 d)	H	60	80	53	52
4 e)	H	60	80	9	0
5 f)	H	60	50	83	73
6 g)	H	60	20	31	22
7 h)	H	30	80	100	91
8 h)	H	15	80	58	54
9 i)	<i>p</i> -CH <sub>3</sub>	60	80	100	100
10	<i>p</i> -Cl	60	100	97	95
11	<i>m</i> -OCH <sub>3</sub>	60	80	100	100

a) A mixture of nitroarene (20 mmol), PtCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.10 mmol), SnCl<sub>4</sub> (2.0 mmol), Et<sub>3</sub>N (1.0 mmol), H<sub>2</sub>O (1 ml) and dioxane (10 ml) was stirred under carbon monoxide for 4h. b) Based on an amount of nitroarene used, by GLC c) PtCl<sub>2</sub>(PhCN)<sub>2</sub> (0.10 mmol) d) Without SnCl<sub>4</sub> e) Without Et<sub>3</sub>N f) Reaction time 7h g) Reaction time 22h h) Nitrobenzene 10 mmol; The ratios of the reactants are the same as in Run 1. i) H<sub>2</sub>O (0.5 ml)

the present catalyst system had no activity for WGSR. These features are quite different from precedents catalyzed by iron, rhodium complexes<sup>1),2)</sup>. The reduction under hydrogen pressure (60 kg/cm<sup>2</sup>) instead of carbon monoxide and water gave 34% yield of aniline, indicating that CO-H<sub>2</sub>O is better hydrogen source in this procedure.

1-Nitropropane, 2-ethyl-2-hexenal, phenylacetylene and diphenylacetylene were not reduced by this procedure. The competitive reduction of nitrobenzene and diphenylacetylene gave only aniline as product, while diphenylacetylene remained unchanged quantitatively. Thus, the present reaction appears to be the chemoselective reduction of nitroarenes.

#### REFERENCES

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