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## Organic Syntheses by Means of Metal Complexes. IV. Reduction of Nitrobenzene with Carbon Monoxide<sup>1)</sup>

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Carbon monoxide has been used to reduce many inorganic compounds, but its use in reduction of organic compounds has not been widely explored. This paper reports the reduction of nitrobenzene with carbon monoxide in acetic acid to give acetanilide.

There are several examples of the reduction of nitrobenzene with carbon monoxide. Formation of azobenzene from nitrobenzene and carbon monoxide has been reported.<sup>2)</sup> Kmiecik<sup>3)</sup> has reported the conversion of 2-nitrobiphenyl to carbazole in the presence of carbon monoxide and iron pentacarbonyl. The synthesis of urethane by the reaction of nitrobenzene and carbon monoxide in alcohols or phenols in the presence of  $\text{Rh}(\text{CO})_2$ -

$\text{Cl}_2$  and co-catalyst is known.<sup>4)</sup> Hardy and Bennett isolated phenylisocyanate by the reaction of nitrobenzene and carbon monoxide in the presence of  $\text{Rh}/\text{C}-\text{FeCl}_3$  catalyst.<sup>5)</sup> In these reactions, carbon monoxide behaves as a reducing agent and carbon dioxide is formed. Phenylnitrene may be considered as an intermediate in these reactions.

We attempted nickel carbonyl catalyzed reduction of nitrobenzene with carbon monoxide, and confirmed the formation of acetanilide in high yield. The reaction should be carried out above 300°C, and at 285°C no acetanilide was obtained. When the reaction was done in propionic acid solution, propionanilide was obtained. Somewhat similar catalytic activities were observed with iron pentacarbonyl and dicobalt octacarbonyl. The results are shown in Table 1. Intramolecular condensa-

1) Part III: Y. Mori and J. Tsuji, *This Bulletin*, **42**, 777 (1969).

2) G. D. Buckley and N. H. Ray, *J. Chem. Soc.*, **1949**, 1154; F. Glaser and R. Van Beneden, *Chem. Ing. Tech.*, **29**, 512 (1957).

3) J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965).

4) Imperial Chemical Industries, Ltd., Brit. Pat. 993704 and 1080094; *Chem. Abstr.*, **64**, 11126h (1966).

5) W. B. Hardy and R. P. Bennett, *Tetrahedron Letters*, **1967**, 961.

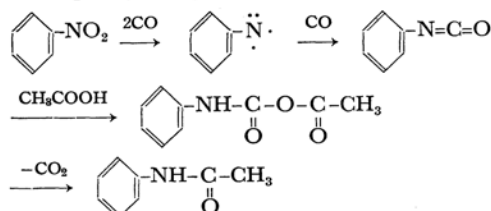
TABLE I. CARBONYLATION OF NITROBENZENE

Nitrobenzene g	RCOOH		Catalyst		CO* kg/cm <sup>2</sup>	Reaction		C <sub>6</sub> H <sub>5</sub> NHCOR g
	R	ml				Temp, °C	Time, hr	
7.4	CH <sub>3</sub>	30	Ni(CO) <sub>4</sub>	1.0 ml	100	310	2.0	5.5
9.0	CH <sub>3</sub>	25	Fe(CO) <sub>5</sub>	1.0 ml	100	310	2.0	6.8
9.0	CH <sub>3</sub>	25	Ni(CO) <sub>4</sub>	0.25 ml	100	310	1.5	6.1
3.6	CH <sub>3</sub>	10	Co <sub>2</sub> (CO) <sub>8</sub>	0.2 g	50	305	2.0	2.5
4.8	C <sub>2</sub> H <sub>5</sub>	25	Ni(CO) <sub>4</sub>	1.0 ml	100	305	2.0	3.1
9.0	CH <sub>3</sub>	25	Ni(CO) <sub>4</sub>	1.0 ml	100	285	2.0	0

\* Initial pressure at room temperature.

tion did not occur with *o*-nitrobenzoic acid in toluene solution and nitrobenzene was obtained by decarboxylation.

This reaction may be explained by the following mechanism. At first nitrobenzene is converted into phenylnitrene by giving the oxygen to carbon monoxide. Phenylnitrene is then carbonylated to produce phenyl isocyanate.



The reaction of isocyanate with acetic acid followed by decarboxylation gives acetanilide. As a related reaction, the formation of acetanilide by the reaction of phenyl thioisocyanate with acetic acid is known.<sup>6)</sup>

### Experimental

**Materials.** Commercially available nickel carbonyl and iron carbonyl were used without further purification. Cobalt octacarbonyl was synthesized from cobalt hydroxide by the known method.<sup>7)</sup> Nitrobenzene was distilled before use.

**Reactions of Nitrobenzene with Carbon Monoxide.** Only a typical experiment is described. A stainless steel autoclave (100 ml) was charged with 9 g of nitrobenzene, 25 ml of acetic acid and 0.25 ml of nickel carbonyl. The autoclave was sealed and pressured to 100 kg/cm<sup>2</sup> with carbon monoxide, and then heated at 310°C for 90 min with stirring. After the reaction, the autoclave was allowed to cool and the reaction product was subjected to distillation. Under reduced pressure, acetanilide (6.1 g, 61%) was collected, which was identified with an authentic sample by mixed melting point determination (112°C) and infrared spectra. At the same time, formation of carbon dioxide was confirmed with a barium hydroxide solution. The other experiments were carried out similarly.

6) B. Pawlewski, *Ber.*, **32**, 1425 (1899).

7) Ajinomoto Co., Inc., Japanese Pat. 265091.