

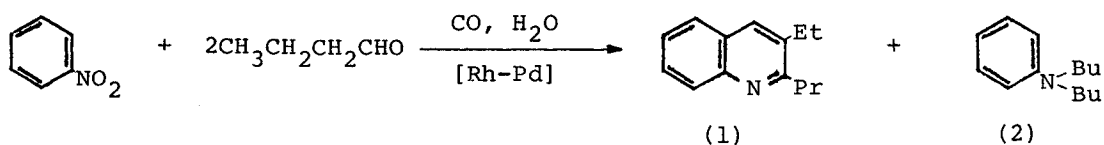
THE TRANSITION METAL-CATALYZED N-ALKYLATION AND N-HETEROCYCLIZATION.
A REDUCTIVE TRANSFORMATION OF NITROBENZENE INTO N,N-DIALKYLANILINE
AND 2,3-SUBSTITUTED QUINOLINE USING ALDEHYDE AND CARBON MONOXIDE

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The catalytic N-alkylation and N-heterocyclization of nitrobenzene occurs at 180°C under pressures of carbon monoxide (70 atm) in the presence of aldehyde and transition metal complexes to give 2,3-dialkyl quinoline and N,N-dialkylaniline in good yields. The product selectivity highly depends on the catalysts.

Reduction of nitroarenes by carbon monoxide using rhodium, palladium, and selenium compounds as catalysts has been currently of interest.¹⁾ Nitroarenes can be converted into a wide variety of useful N-containing compounds such as aminoarenes,^{1a)} diarylureas,^{1b)} aryl isocyanates,^{1c)} and alkyl carbanilates.^{1d)}

In this communication, we wish to report the selective transformation of nitrobenzene to substituted quinoline or N,N-dialkylaniline by the rhodium and/or palladium catalyzed reduction with carbon monoxide in the presence of an aldehyde. The rhodium-catalyzed reaction between aminoarenes and aliphatic aldehydes has been shown to lead to a novel, non-acidic pathway to N-heterocyclization.²⁾



Typically, a mixture of nitrobenzene (40 mmol), butanal (90 mmol), water (2 ml), ethanol (20 ml), and a rhodium (0.03-0.12 mmol) and/or a palladium complex (0.03-0.12 mmol) in a 100 ml autoclave was stirred under pressures of carbon monoxide (initial pressure, 70 atm) at 180°C for 4 h. Products were isolated by vacuum distillation and analyzed by means of IR and NMR spectra.

Nitrobenzene combined with butanal in this procedure gave 2-propyl-3-ethylquinoline (1) or N,N-dibutylaniline (2). Typical results are listed in Table. The products highly depended on the catalysts. The reaction catalyzed by chlorotris(triphenylphosphine)rhodium gave (1) exclusively, and that catalyzed by μ, μ' -dichlorobis(norbornadiene)dirhodium gave (2), while rhodium trichloride gave a mixture of (1) and (2). The catalytic selectivity of $[\text{RhCl}(\text{NBD})]_2$ was changed by addition of triphenylphosphine to be favorable for formation of (1). Accordingly, (1) and (2) can be selectively prepared by this method from nitrobenzene and butanal. An attempt

Table. The transition metal-catalyzed N-alkylation and N-heterocyclization of nitrobenzene^{a)}

Run	Catalyst ^{b)}	Conversion ^{c)} (%)	Product ^{d)}		Yield ^{c)} (2)	Product Selectivity ^{e)}		
			(1)	(%)		(1)	(%)	(2)
1	A(0.03 mmol)	55	7		28	12		51
2	B(0.03)	51	11		~0	22		~0
3	C(0.03)	37	~0		28	~0		76
4 ^{f)}	C(0.03)	64	~0		47	~0		73
5	B(0.03) + D(0.03)	67	25		~0	38		~0
6	B(0.03) + D(0.09)	76	44		~0	63		~0
7	B(0.06) + D(0.09)	82	60		~0	72		~0
8	C(0.06) + D(0.09)	~100	15		46	15		46
9	D(0.05)	23	10		~0	41		~0

a) A mixture of nitrobenzene(40 mmol), butanal(90 mmol), water(2 ml), a rhodium and/or palladium complex, and ethanol(20 ml) was treated at 180°C under pressures of carbon monoxide(70 atm) for 4 h.

b) A, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$; B, $\text{RhCl}(\text{PPh}_3)_3$; C, $[\text{RhCl}(\text{NBD})]_2$; D, PdCl_2 .

c) Based on an amount of nitrobenzene used. Determined by GLC.

d) (1), 2-propyl-3-ethylquinoline; (2), N,N-dibutylaniline.

e) Based on an amount of nitrobenzene converted.

f) The reaction time, 8 h.

to prepare (2) from aniline and butanal was unsuccessful: the rhodium(even $[\text{RhCl}(\text{NBD})]_2$)-catalyzed reaction between aniline and butanal gives (1) in excellent yields. Thus, formation pathways should be different between (1) and (2): via aniline for (1) and a nitrene or other for (2). A nitrene intermediate has been proposed for reduction of nitroarenes with carbon monoxide.¹⁾

The catalytic activity and selectivity were highly improved by using a binary catalyst. A binary catalyst, $\text{RhCl}(\text{PPh}_3)_3$ and PdCl_2 , gave excellent conversion and fairly good yield of (1) (Run 7). The combination, $[\text{RhCl}(\text{NBD})]_2$ and PdCl_2 , gave 100% conversion but poorer selectivity (Run 8).

The results obtained here demonstrate that this procedure is applicable for synthesis of substituted quinolines and N,N-dialkyl aminoarenes from nitroarenes and aliphatic aldehydes.

References

- 1) See, for example: a) A.F.M. Iqbal, US 3,944,615; C.A., 85, 20814(1976); J. Org. Chem., 37, 2791(1972); b) H.A. Dieck, R.M. Laine, and R.F. Heck, J. Org. Chem., 40, 2819(1975); c) F.J. Weigert, J. Org. Chem., 38, 1316(1973); W.B. Hardy and R.P. Bennett, Tetrahedron Lett., 961(1967); T. Yamahara, T. Deguchi, S. Inokuma, and S. Nakamura, Japan Kokai, 75,112,322; C.A., 83, 205915(1975); d) US Appl., 459,998; C.A., 84, 30723(1976); H. Yutaka, M. Katsuharu, and M. Aiga, Ger. Offen., 2,603,574; C.A., 85, 123,648(1976).
- 2) Y. Watanabe, M. Yamamoto, S.C. Shim, T. Mitsudo, and Y. Takegami, Chem. Lett., 1025(1979).

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