Application of the Water-gas Shift Reaction. III. Reduction of Oxidized Nitrogen Compounds with CO and H_2O Catalyzed by $[Ru(cod)py_4](BPh_4)_2$

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Synopsis. The ruthenium(II) complex, $[Ru(cod)py_4](BPh_4)_2$ (cod=1,5-cyclooctadiene, py=pyridine) has been shown to catalyze the reduction of oxidized nitrogen compounds with CO and H_2O. In this reaction, primary, secondary, and tertiary nitroalkanes are converted into amides, ketones, and amines, respectively. Nitrosobenzene and picoline *N*-oxides are also reduciable to amines in good yields.

Much attention has been devoted to the reduction of organic molecules with CO and H_2O without using molecular hydrogen. The reduction of nitrobenzenes with this system has been thoroughly investigated,[1-3] yet the reductions of other compounds have rarely been known.[4-5] We have previously reported that the ionic ruthenium(II) complex, $[Ru(cod)py_4](BPh_4)_2$ (**1**), is an efficient catalyst for the reduction of nitrobenzenes with CO and H_2O. In this paper, we describe the application of this catalytic system to the reduction of some compounds containing oxidized nitrogen.

Unlike the reduction of nitrobenzenes, 1-nitropropane reacted with CO and H_2O in the presence of **1** to give mainly propionamide. Small amounts of propionitrile and propylamine derivatives such as $CH_3CH_2CH_2NHCOCH_2CH_3$ and $(CH_3CH_2CH_2)_2NCHO$ were formed as organic by-products, but propylamine was not detected. As an inorganic product a small quantity of ammonium hydrogencarbonate was found. For this reaction the presence of both CO and H_2O was essential. However, either the presence of a large excess of H_2O or the application of a high pressure of CO resulted in decrease in the yield of the amide but increase in the formation of ammonium hydrogencarbonate. The favorable reaction conditions were as follows: CO=15 atm, $H_2O/RNO_2=2$ mol/mol. 1-Nitrohexane was similarly reduced to the corresponding amide and nitrile.

Interestingly, the reaction of secondary nitroalkane, 2-nitropropane, gave acetone and acetone oxime. This oxime formation suggests that oximes may be one of the intermediates in the reaction of primary and secondary nitro compounds. In fact, under these conditions acetone oxime was hydrolyzed to acetone in 66% yield. Propionaldehyde oxime was also converted into a mixture of propionamide (63%) and propionitrile (4%). This is the Beckmann rearrangement of aldoxime, which has been known to be catalyzed by some transition metal complexes.[6] For this reaction, neither CO nor H_2O was needed, while the product ratio was affected; the yield of propionitrile was increased up to 47% in the absence of CO and H_2O, whereas propionamides was formed in 36% yield.

Table 1. Reduction of nitroalkanes with CO and H_2O catalyzed by $[Ru(cod)py_4](BPh_4)_2$[a)]

Sub. (RNO_2) R–	CO (atm)	Products (Yield /%)[b)]				
$CH_3CH_2CH_2$–	10	$CH_3CH_2CONH_2$ (47)	CH_3CH_2CN (1)	$CH_3CH_2CH_2NHCOCH_2CH_3$ (1)	$(CH_3CH_2CH_2)_2NCHO$ (1)	NH_4CO_3H (≈0)
$CH_3CH_2CH_2$–	15	$CH_3CH_2CONH_2$ (54)	CH_3CH_2CN (1)	$CH_3CH_2CH_2NHCOCH_2CH_3$ (2)	$(CH_3CH_2CH_2)_2NCHO$ (4)	NH_4CO_3H (≈0)
$CH_3CH_2CH_2$–	50	$CH_3CH_2CONH_2$ (32)	CH_3CH_2CN (1)	$CH_3CH_2CH_2NHCOCH_2CH_3$ (2)	$(CH_3CH_2CH_2)_2NCHO$ (3)	NH_4CO_3H (56)[c)]
$CH_3CH_2CH_2$–	80	$CH_3CH_2CONH_2$ (11)	CH_3CH_2CN (1)	$CH_3CH_2CH_2NHCOCH_2CH_3$ (2)	$(CH_3CH_2CH_2)_2NCHO$ (2)	NH_4CO_3H (23)[c)]
$CH_3CH_2CH_2$–[d)]	15	$CH_3CH_2CONH_2$ (48)	CH_3CH_2CN (1)	$CH_3CH_2CH_2NHCOCH_2CH_3$ (2)	$(CH_3CH_2CH_2)_2NCHO$ (1)	NH_4CO_3H (2)[c)]
$CH_3(CH_2)_5$–	15	$CH_3(CH_2)_4CONH_2$ (42)	$CH_3(CH_2)_4CN$ (8)	NH_4CO_3H (11)[c)]		
$(CH_3)_2CH$–	15	CH_3COCH_3 (58)	$(CH_3)_2C{=}NOH$ (15)	NH_4CO_3H (34)[c)]		
$(CH_3)_3C$–[e)]	50	$(CH_3)_3CNH_2$ (63)	NH_4CO_3H (≈0)			

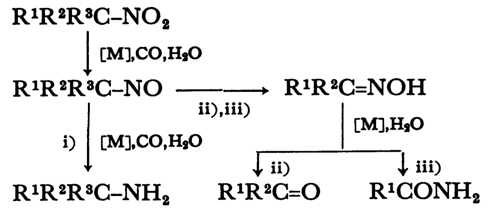
a) Reaction conditions: complex **1** (0.1 mmol), substrate (20 mmol), H_2O (40 mmol), THF (5 ml), 140 °C, 20 h. b) The yields were determined by GC using internal standards. c) Isolated yields. d) H_2O (100 mmol) was used. e) At 170 °C.

Table 2. Catalytic reduction of oxidized nitrogen compounds

Substrate	Condition[a)]	Product	Yield/%[b)]
Nitrosobenzene	A	Aniline	82
β-Picoline *N*-oxide	A[c)]	*β*-Picoline	89
γ-Picoline *N*-oxide	A[c)]	*γ*-Picoline	99
m-Nitrobenzonitrile	B	*m*-Aminobenzonitrile	93
m-Nitroacetophenone	B	*m*-Aminoacetophenone	81
m-Nitrobenzaldehyde	B	Poly(nitrilo-1,3-phenylenemethylidyne)	100[d)]

a) Condition A: complex **1** (0.2 mmol), substrate (20 mmol), H_2O (40 mmol), THF (5 ml), CO (50 atm), 100 °C, 20 h; Condition B: complex **1** (0.05 mmol), substrate (10 mmol), H_2O (20 mmol), THF (5 ml), CO (50 atm), 150 °C, 20 h. b) GC yields. c) H_2O was not used. d) Isolated yield.

On the other hand, the reaction of 2-nitro-2-methylpropane gave *t*-butylamine exclusively. The difference between tertiary and secondary or primary nitroalkanes seems to be attributed to the hydrogens on the *α*-carbon atom. It may be deduced that at the first stage of the catalysis a nitroso compound is formed as an intermediate. Actually, nitrosobenzene was readily reduced to aniline in a high yield compared with the reduction of nitrobenzene (76%). The reaction scheme is illustrative as follows.



i) R^1,R^2,R^3 = alkyl. ii) R^1,R^2 = alkyl, R^3 = H.
iii) R^1 = alkyl, R^2,R^3 = H.

The applications of the catalyst **1** to the reductions or various organic compounds such as 1-hexane, methyl cinnamate, acetophenone, benzonitrile, *N*-benzylidenecyclohexylamine, triphenylphosphine oxide, and diphenyl sulfone were attempted, but these compounds were virtually inert under Condition A shown in Table 2. Picoline *N*-oxides were exceptionally reduciable to picolines, though the presence of H_2O is not required. These results indicate that the catalysis of **1** is selective to the reduction of compounds containing oxidized nitrogen. Consequently, it was possible to achieve the selective reduction of the nitro group of substituted nitrobenzenes containing cyano or carbonyl group.

Experimental

GC-MS spectra were recorded on a Hitachi M-52 spectrometer. ^1H-NMR spectra were recorded with a Varian T-60A spectrometer. All liquid compounds were distilled under an atmosphere of nitrogen before use.

General Procedure. All reactions were carried out in a stainless steel autoclave of 65 ml capacity, heated by an external rocking electric oven. A THF solution of $[Ru(cod)py_4](BPh_4)_2$, substrate, and H_2O was placed in the autoclave, which was subsequently charged with CO. After heating for 20 h, the autoclave was cooled to room temperature. The reaction mixture was analyzed by the GC method using an internal standard. The identification of the products was accomplished by GC/MS, IR, and ^1H-NMR techniques, and by comparison with those of authentic samples. Some spectral data were as follows; $CH_3CH_2CH_2NHCOCH_2CH_3$: MS, 115 (M^+); IR (cm^{-1}), 3350 (ν_{NH}), 1640 (ν_{CO}); ^1H-NMR (CCl_4, δ), 0.9 (t, CH_3CCN), 1.5 (h, CH_2CN), 3.1 (q, CH_2N), 1.1 (t, CH_3CCO), 2.2 (q, CH_2CO), 7.6 (b, NH); $(CH_3CH_2CH_2)NCHO$: MS, 129 (M^+); IR (cm^{-1}), 1660 (ν_{CO}); ^1H-NMR (CCl_4, δ), 0.9 (t, CH_3), 1.5 (h, CH_2CN), 3.2 (t, CH_2N), 8.0 (s, CHO).

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