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CuCl-catalyzed Oxidative Coupling Reaction of Secondary Amines with Molecular Oxygen in Pyridine

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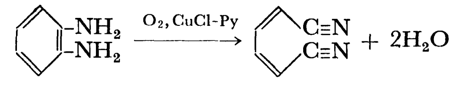
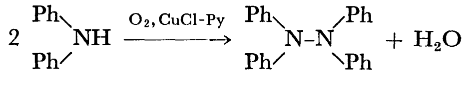
Synopsis. Oxidation of diphenylamine with molecular oxygen in the presence of CuCl in pyridine at room temperature to give tetraphenylhydrazine in a high yield was achieved by selecting suitable reaction conditions. *N*-methylaniline was also oxidized to give *N,N′*-dimethyl-*N,N′*-diphenylhydrazine.

In a previous paper we reported a unique oxidation of *o*-phenylenediamine with molecular oxygen in the presence of CuCl in pyridine at room temperature to give *cis,cis*-muconontrile.[1] The most important factor in this reaction is the ratio of *o*-phenylenediamine to CuCl in the reaction medium and the ratio should be kept less than 0.5 (mol/mol) to obtain the nitrile in a high yield. A suitable procedure for this is the dropwise addition of a solution of the diamine in pyridine to a solution of CuCl. In this paper a successful application of this catalyst system to the oxidation of secondary amines to tetrasubstituted hydrazines is reported.



Results and Discussion

Copper(I) chloride is slightly soluble in pyridine under an inert atmosphere at room temperature, but a mixture of CuCl and pyridine absorbs oxygen with stirring under oxygen atmosphere to give a deep green solution. One mol of oxygen is absorbed per four atoms of copper. From this solution an oxygen complex was precipitated by addition of diethyl ether and its elemental analysis supported a composition of $(CuCl)_4(C_5H_5N)_4O_2$.[1] When a pyridine solution of diphenylamine (0.5 molar equiv. to CuCl) was added slowly to a pyridine solution of CuCl pretreated with oxygen, further absorption of oxygen was observed showing that the oxidation took place. The amount of oxygen absorbed during the oxidation was 0.6 molar equivalent to diphenylamine added, and after usual work-up tetraphenylhydrazine was obtaine in 83% yield.



$$2\,Ph_2NH \xrightarrow{O_2,\,CuCl\text{-}Py} Ph_2N\text{-}NPh_2 + H_2O$$

N-methylaniline was also oxidized to give *N,N′*-dimethyl-*N,N′*-diphenylhydrazine in 52%. From other secondary amines such as di-2-naphthylamine and *N*-ethylaniline the corresponding hydradines were not obtained in high yields though similar absorption of oxygen was observed.

A probable reaction mechanism is shown as follows.

$$CuCl \xrightarrow{O_2,\,Py} \underset{\mathbf{1}}{(CuCl)_4(Py)_4O_2} \xrightarrow{O_2,\,R_1R_2NH}$$

$$\underset{\mathbf{2}}{(CuCl)_2(R_1R_2NH)_2(Py)_mO_2} \longrightarrow$$

$$\underset{\mathbf{3}}{(CuCl)_2(R_1R_2N\cdot)_2(Py)_xO_y\cdot H_2O}$$

$$\xrightarrow{O_2,\,Py} R_1R_2N\text{-}NR_1R_2 + H_2O + \underset{\mathbf{1}}{(CuCl)_4(Py)_4O_2}$$

Coupling of amino radicals in the coordination sphere of complex **3** gives the hydrazine. When the concentration of the secondary amine in the reaction medium is so high to substitute more pyridines coordinated in the complex **2**, the amino radical may attack another secondary amine coordinated to give by-products such as oligomer and polymer of the amine. The low yield of hydrazine from di-2-naphthylamine may be attributed to the instability of di-2-naphthylamino radical.[2]

The unique oxidation method with CuCl in pyridine is thus useful for the oxidative coupling reaction of secondary amines to give tetrasubstituted hydrazine as well as other oxidation methods with PbO_2 or $KMnO_4$.[3]

Experimental

Melting points are uncorrected. Infrared spectra were recorded on a Shimadzu Model IR-27 infrared spectrophotometer, and nuclear magnetic resonance spectra on a Varian HA-100 (100 MHz) and a Varian A-60 (60 MHz) using tetramethylsilane as an internal standard in $CDCl_3$. All metal salts and secondary amines were obtained commercially.

General Procedure of Oxidation. Copper(I) chloride and pyridine were added in a glass flask immersed in a water bath under argon atmosphere with vigorous stirring and then the atmosphere was replaced with oxygen. After the absorption of oxygen ceased, the secondary amine in pyridine was added slowly with further absorption of oxygen. The amount of oxygen absorbed was measured with a gas buret. Pyridine was distilled off under reduced pressure after the reaction, and the residue was extracted with ether to give a crude product which was subjected to column chromatographic purification.

Tetraphenylhydrazine. Diphenylamine (1.69 g) in 10 ml of pyridine was treated with CuCl (1.98 g) in 50 ml of pyridine and the crude product was chromatographed on an alumina column with benzene–petroleum ether (1:1) to give tetraphenylhydrazine (1.4 g, 83%), mp 146.5 °C (lit,[3] mp 144.5 °C). The IR spectrum was identical with that of an authentic sample. Found: C, 86.03; H, 5.27; N, 8.11%. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33%.

N,N′-*Dimethyl*-N,N′-*diphenylhydrazine.* *N*-Methylaniline (1.07 g) in 10 ml of pyridine was treated with CuCl (1.98 g) in 50 ml of pyridine and distillation of the crude product gave *N,N′*-dimethyl-*N,N′*-diphenylhydrazine (0.6 g,

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52%), bp 160 °C/4 mmHg. The IR spectrum was identical with that of an authentic sample. ^{1}H NMR ($CDCl_3$): δ= 2.90(6H, s), 6.5—7.5 (10H, m). Found: C, 79.15; H, 7.56; N, 13.35%. Calcd for $C_{14}H_{16}N_2$: C, 79.21; H, 7.60; N, 13.20%.

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