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Efficient Catalytic Oxidation of Primary Aromatic Amines to Azo Derivatives by Manganese(III) Tetraphenylporphyrin†

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The oxidation of primary aromatic amines to the corresponding azo derivatives has been observed in catalytic systems containing manganese(III) tetraphenylporphyrin and sodium periodate in the presence of heterocyclic nitrogen bases acting as axial ligands.

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The catalytic role of metallo-porphyrins for hydroxylation of alkanes,[1,2] epoxidation of alkenes,[3,4] demethylation of *N*-methylbenzylamine,[5] oxidation of nitroso[6] and primary aromatic amines[7–10] to nitro derivatives has been observed. In this report, we describe a periodate-metalloporphyrin system for oxidation of primary aromatic amines to azo derivatives.

One important aspect of this catalytic system is the modification of the oxidation rate by addition of a small amount of imidazole to the mixture. The corresponding results of the effect of various axial ligands on oxidation of *para*-toluidine are presented in Table 1. The formation of azo product in the absence of axial ligand is very slow and the yields are always below 10% within 90 min, whereas 100% GLC yield of azo product is obtained during the same period in the catalyzed reaction with imidazole as the axial ligand. The yield of azo product in the oxidation of *para*-toluidine decreased in the following order using different axial ligands: imidazole ≫ 4-methylpyridine > 2-methylpyridine > pyridine.

Reactions were performed at room temperature in air in CH_2Cl_2–H_2O containing the primary aromatic amines, periodate, axial ligand and tetraphenylporphyrinatomanganese(III) chloride (MnTPPCl) in 83:166:17:1 ratios, respectively. This catalytic system led to oxidation of primary aromatic amines $RC_6H_4NH_2$ **1**–**13** to azo derivatives (**1a**–**13a**) (Scheme 1) in good isolated yields (38–85%) (Table 2).

$$\underset{\mathbf{1-13}}{RC_6H_4NH_2} \xrightarrow[CH_2Cl_2-H_2O,\ \text{Imidazole},\ Bu_4NBr]{\text{MnTPPCl},\ NaIO_4,\ \text{room temp.}} \underset{\mathbf{1a-13a}}{RC_6H_4N{=}NC_6H_4R}$$

1 R = *p*-Et
2 R = *p*-Me
3 R = *o*-Me
4 R = *p*-OMe
5 R = *o*-OMe
6 R = *m*-OMe
7 R = H
8 R = *o*-CN
9 R = *o*-Cl
10 R = *p*-NO_2
11 R = *m*-NO_2
12 R = *o*-NO_2
13 R = *p*-Br

Scheme 1

Control experiments carried out on the amines showed that, in the absence of catalyst, no oxidation to azo compounds occurs.

The effect of axial ligands clearly indicate that an electron donating axial substituent coordinated to the metal is essential for the above oxidation of primary aromatic amines with MnTPPCl as catalyst. The highest coordinative capability of imidazole compared to other axial ligands and amines is shown by the pronounced spectral changes of the MnTPPCl Soret band at 477.5 nm in the presence of imidazole.

Table 1 Effect of various axial ligands on oxidation of *para*-toluidine to azo product in 90 min[a]

Axial ligand	Azo yield (%)[b]	Turnover per h
Imidazole	100	55.55
4-Methylpyridine	25	13.88
2-Methylpyridine	19	10.55
Pyridine	12	6.67
Without axial ligand	10	5.55

[a]Reaction conditions: *para*-toluidine (1 mmol), MnTPPCl (0.012 mmol), axial ligand (0.2 mmol), $NaIO_4$ (2 mmol), tetrabutylammonium bromide (0.05 mmol), CH_2Cl_2/H_2O (10 ml/10 ml). [b]GLC yields based on starting *para*-toluidine.

The oxidation product of benzylamine under the above conditions was benzaldehyde with 90% isolated yield and 100% selectivity.

Experimental

MnTPPCl was prepared according to the literature procedures.[11,12] In a typical reaction, a 50 ml flask was charged with primary aromatic amine (1 mmol), MnTPPCl (0.012 mmol), imidazole (0.2 mmol), CH_2Cl_2 (10 ml), $NaIO_4$ (2 mmol) in H_2O (10 ml) and 0.05 mmol of tetrabutylammonium bromide as a phase transfer catalyst. The reaction was magnetically stirred at room temperature for 1–5 h. The progress of the reaction was monitored by gas chromatography and the products were separated by column chromatography with silica gel. All the oxidation products were clearly identified by IR, ^1H NMR and UV–VIS spectral data.

Table 2 Oxidation of primary aromatic amines (**1**–**13**) to azo derivatives (**1a**–**13a**) with $NaIO_4$ catalyzed by MnTPPCl in the presence of imidazole[a]

Amine	Azo yield (%)[b]	Reaction time/h
1	85	2
2	80	1
3	80	2
4	80	1.5
5	80	2
6	80	3
7	70	2
8	60	3
9	50	4
10	48	5
11	63	5
12	40	5
13	38	1.5

[a]Reaction conditions: aromatic amine (1 mmol), MnTPPCl (0.012 mmol), axial ligand (0.2 mmol), $NaIO_4$ (2 mmol), tetrabutylammonium bromide (0.05 mmol), CH_2Cl_2/H_2O (10 ml/10 ml). [b]Isolated yields based on starting aromatic amine.

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