Catalytic Oxidation of Primary Aromatic Amines to the Corresponding Nitroso Compounds by H_2O_2 and $[Mo(O)(O_2)_2(H_2O)(hmpa)]$ (hmpa = Hexamethylphosphoric Triamide)

Stefano Tollari, Michaela Cuscela and Francesca Porta*

Dipartimento di Chimica Inorganica, Metallorganica e Analitica, e Centro CNR, Università di Milano, Via Venezian 21, 20133 Milano, Italy

$[Mo(O)(O_2)_2(H_2O)(hmpa)]$ **1** catalyses the oxidation of primary aromatic amines to the corresponding nitroso derivatives, in the presence of H_2O_2 as oxidant.

So far, few metal-catalysed methods reported in the literature[1] are able to yield aromatic nitroso compounds. Moreover, organic synthetic methods have not yet provided an easy and mild path to obtain these interesting compounds.[2] It is known that complex **1** is able to transfer one peroxidic oxygen atom to an olefin to yield epoxides;[3] these reactions can become catalytic using H_2O_2 as oxidant.[4] We have already reported that aliphatic primary amines are catalytically oxidized to the corresponding oximes and Schiff bases by **1** in the presence of H_2O_2.[5] The coordination chemistry of *C*-nitroso compounds has been extensively researched[6] as well as the imido-transfer reactions of nitroso-arene complexes with alkenes.[7]

We present herein a new catalytic reaction which results in the selective oxidation of primary aromatic amines **2–19** to the corresponding nitroso derivatives using **1** as catalyst and H_2O_2 as oxidant [eqn. (1)]

$$RC_6H_4NH_2 \xrightarrow[H_2O_2]{1} RC_6H_4NO \qquad (1)$$

$$\mathbf{1} = [Mo(O)(O_2)_2(H_2O)(hmpa)]$$

R = H(2); *p*-CH_3(3); *p*-CH_3CH_2(4); *p*-$C(CH_3)_3$(5); *p*-OCH_3(6); *p*-CH_3COO(7); *p*-CH_3CONH(8); *p*-F(9); *p*-Cl(10); *p*-Br(11); *m*-CH_3(12); *m*-Cl(13); *m*-OCH_3(14); *o*-CH_3(15); *o*-CH_3CH_2(16); *o*-OCH_3(17); *p*-NO_2(18); *m*-CF_3(19).

At room temperature, in CH_2Cl_2 (5 ml) and under nitrogen, total conversion of **2–17** is achieved after 14–72 h, while the yields of 2a–17a range between 40 and 80%† (see Table 1). The amines **18** and **19**, which have electron-withdrawing ring substituents, do not react. The products, detected by gas chromatography–mass spectrometry and gas chromatography, were quantified after work-up of the solution and separation by flash chromatography.‡ Aerobic treatment of the reaction mixture does not modify the nature and/or the amounts of the products obtained; among these, only the nitroso derivatives **2a–18a** were quantified.

In a few cases, small amounts (*ca.* 2 and 3%, respectively) of the corresponding azo and azoxy derivatives were detected. A blank experiment on **3** showed that, in the absence of the catalyst **1**, no oxidation occurs and the amine was unchanged.

In order to obtain the highest yields of the nitroso derivatives **2a–17a** it is necessary to avoid the possible subsequent oxidation to the corresponding nitro derivatives, by frequent checking of the reaction profile, and by stopping the reaction immediately after the amine has been completely consumed. The procedure given‡ and the reaction times listed in Table 1 represent the conditions for obtaining the best yields of **2a–17a** (amine conversion: 100%; yields of the corresponding nitro derivatives zero). The use of different solvent (MeCN or $CHCl_3$), or different work up procedures gave lower yields.

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† All compounds **2a–18a** have been characterized by IR, ^1H NMR, mass spectrometry and m.p.

‡ Representative procedure: the amine (1 mmol) and H_2O_2 (0.5 ml of a 30% w/w solution in water; 5 mmol) are added to a CH_2Cl_2 solution (5 ml) containing 0.1 mmol of **1** under a nitrogen atmosphere. At the end of the reaction, after the addition of Na_2SO_4 and 10 ml of solvent, the mixture was filtered and the filtrate evaporated to dryness. The crude product was purified by flash chromatography over silica (hexane–CH_2Cl_2, 4 : 6).

Table 1 Yields of nitroso derivatives from catalytic oxidation of the aromatic amines **2–19** by **1** and H_2O_2[a]

R-$C_6H_4NH_2$	Yields of **2a–19a** (%)	t/h
R = H	77.7	16
p-Me	73.0	18
p-Et	80.7	18
p-Bu^t	83.5	16
p-OMe	75.4	18
p-CO_2Me	79.3	72
p-NHCOMe	49.6	16
p-F	81.2	16
p-Cl	79.6	26
p-Br	76.2	72
m-Me	42.1	20
m-Cl	58.6	72
m-OMe	72.7	18
o-Me	65.0	17
o-Et	79.7	14
o-OMe	76.7	36
p-NO_2	10	72
m-CF_3	—	72

[a] **1**, 0.1 mmol; H_2O_2, 5 mmol; **2–19**, 1 mmol; solvent, CH_2Cl_2 (5 ml). Yields are for isolated nitroso derivatives **2a–18a**. The conversion is 100% for the amines **2–17**.

The nitroso derivatives obtained in this way are mixtures of monomeric and dimeric compounds (not quantified). The IR spectra in KBr of **2a–17a** showed a weak band close to 1500 cm^{-1}, attributable to the stretching mode of the N=O bond of the monomer, while a band of medium intensity in the 1300—1250 cm^{-1} region corresponds to the stretching mode of the nitrogen–oxygen double bond of the dimer in the more stable *trans*-configuration. These assignments are in agreement with reported values.[8]

The oxidation path of this reaction could follow the steps: amine → hydroxylamine → nitroso, in which the oxygenation of the nitrogen atom of the substrate is accomplished by the formation of an oxo molybdenum complex, originating from nucleophilic attack of the amine onto a peroxidic oxygen or SET processes.[9] Early literature reports and a recent communication on this subject support this hypothesis.[7]

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