

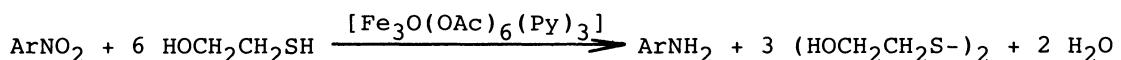
$\text{Fe}_3\text{O}(\text{OAc})_6(\text{Py})_3$  Mediated Reduction of Aromatic Nitro Compounds  
with 2-Mercaptoethanol

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Aromatic nitro compounds were selectively reduced by 2-mercaptoproethanol in the presence of  $\text{Fe}_3\text{O}(\text{OAc})_6(\text{Py})_3$  to give the corresponding amines in good yields.

Oxo-centered triiron carboxylate complexes of the formula  $[\text{Fe}_3\text{O}(\text{OCOR})_6\text{L}_3]^{n+}$  ( $\text{L}$ =neutral ligand,  $n=0$  or  $1$ ) have been recently attracted considerable attention, since they exhibit interesting physical properties<sup>1)</sup> and work as unique catalysts for oxygenation of alkynes,<sup>2)</sup> alkanes,<sup>3)</sup> and amides,<sup>4)</sup> these complexes being regarded as simple models for active sites of certain iron-containing proteins in biology.<sup>5)</sup>

We now report that an iron complex  $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{OAc})_6(\text{Py})_3]$  (1) can effectively mediate the reduction of aromatic nitro compounds with a thiol to give the corresponding amines.<sup>6)</sup> This is the first example, to our knowledge, of application of such a complex to a reduction catalyst.



Treatment of 1-nitronaphthalene (3) (1 mmol) with 2-mercaptoproethanol (2) (8 mmol) in pyridine (10 ml) in the presence of the iron complex 1 (0.05 mmol) with stirring at room temperature under nitrogen for 18 h gave 1-naphthylamine (4) (97%) together with 2-hydroxyethyl disulfide (95%).<sup>7)</sup> While thiophenols and n-alkanethiols could be also used, among the thiols tested 2 gave the most satisfactory result for the reaction rate. Several related mixed trinuclear acetate complexes along with some di- and mononuclear iron complexes and simple iron salts were also examined for the catalyst (Table 1). In a series of  $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{OAc})_6(\text{Py})_3]$  ( $\text{M}=\text{Mn, Fe, Co, and Ni}$ ), the order of activity on the basis of the results for the conversion was found to follow the sequence  $\text{Fe} \approx \text{Mn} > \text{Ni} > \text{Co}$ .  $[\text{Fe}^{\text{III}}_3\text{O}(\text{OAc})_6(\text{Py})_3]\text{ClO}_4$  was also highly active. The other iron species tested appeared to be less effective than 1. A more polar solvent *N,N*-dimethylformamide (DMF) was found to enhance the reaction rate and to be synthetically useful; the reaction was completed for a period of 5 h and the amine 4 was obtained in an almost pure state after extraction with ether and washing with water.

Table 2 shows the results for reduction of 2- or 4-substituted nitrobenzenes (5) in DMF. Both aldehyde and ketone groups were not reduced and the corresponding amines (6) were formed cleanly. Somewhat longer time or higher temperature was needed to complete the reaction of the substrate having either

Table 1. Reduction of 1-nitronaphthalene<sup>a)</sup>

Fe complex	Yield of 4 / % <sup>b)</sup>	Recov. of 3 / % <sup>b)</sup>
[Fe <sup>III</sup> ] <sub>2</sub> Fe <sup>II</sup> O(OAc) <sub>6</sub> (Py) <sub>3</sub>	97	
[Fe <sup>III</sup> ] <sub>2</sub> Mn <sup>II</sup> O(OAc) <sub>6</sub> (Py) <sub>3</sub>	99	
[Fe <sup>III</sup> ] <sub>2</sub> Co <sup>II</sup> O(OAc) <sub>6</sub> (Py) <sub>3</sub>	38	57
[Fe <sup>III</sup> ] <sub>2</sub> Ni <sup>II</sup> O(OAc) <sub>6</sub> (Py) <sub>3</sub>	63	30
[Fe <sup>III</sup> ] <sub>3</sub> O(OAc) <sub>6</sub> (Py) <sub>3</sub> ]ClO <sub>4</sub>	96	
[Fe(Salen)] <sub>2</sub> O <sup>c)</sup>	54	45
[Fe(TPP)] <sub>2</sub> O <sup>d)</sup>	7	91
[Fe(TPP)]OAc <sup>e)</sup>	28	70
FeCl <sub>2</sub> ·4H <sub>2</sub> O	11	88
FeSO <sub>4</sub> ·7H <sub>2</sub> O	12	87

a) The reaction was carried out in pyridine at room temperature under nitrogen for 18 h. [Fe complex]:[3]:[2]=0.05:1:8.  
b) Determined by GLC. c) Salen=N,N'-bis-(salicylidene)ethylenediaminato. d) TPP=meso-tetraphenylporphyrinato.  
e) [Fe complex]=0.15.

an electron donating group or an ortho-substituent.

The present system using 1 and 2 could also be applied to reductions of benzil to benzoin (95%) and azobenzene to hydrazobenzene (80%).

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- 7) It was confirmed that FT-IR spectrum of the recovered complex (71%) by adding ether to the reaction mixture under the conditions using stoichiometrically a slight excess amount of 3 (2:3=5:1) was identical with that of 1.
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Table 2. Reduction of substituted nitrobenzenes<sup>a)</sup>

Substituent	Yield of 6 / % <sup>b)</sup>	Recov. of 5 / % <sup>b)</sup>
4-MeCO	99	
4-Cl	99	
H <sup>c)</sup>	70	22
4-Me	54	45
4-Me <sup>c)</sup>	99	
4-MeO	27	60
4-MeO <sup>d)</sup>	97	
2-CHO	99	
2-Cl	90	7

a) The reaction was performed in DMF at room temperature under nitrogen for 18 h. [1]:[2]:[3]=0.05:1:8. b) Determined by GLC. c) At 50 °C. d) Reaction for 60 h.

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