

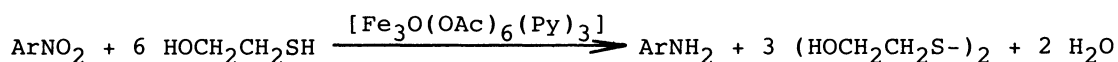
$\text{Fe}_3\text{O}(\text{OAc})_6(\text{Py})_3$ Mediated Reduction of Aromatic Nitro Compounds
with 2-Mercaptoethanol

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Aromatic nitro compounds were selectively reduced by
2-mercaptoethanol 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 $[\text{Fe}_3\text{O}(\text{OCOR})_6\text{L}_3]^{n+}$ (L=neutral ligand, n=0 or 1) have been recently attracted considerable attention, since they exhibit interesting physical properties¹⁾ and work as unique catalysts for oxygenation of alkenes,²⁾ alkanes,³⁾ and amides,⁴⁾ these complexes being regarded as simple models for active sites of certain iron-containing proteins in biology.⁵⁾

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.⁶⁾ 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-mercaptoethanol (**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-hydroxyethylthiyl disulfide (95%).⁷⁾ 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 $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{OAc})_6(\text{Py})_3]$ (M=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^{a)}

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

Table 2. Reduction of substituted nitrobenzenes^{a)}

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

a) The reaction was performed in DMF at room temperature under nitrogen for 18 h. [1]:[5]:[2]=0.05:1:8. b) Determined by GLC. c) At 50 °C. d) Reaction for 60 h.

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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