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$Fe_3O(OAc)_6(Py)_3$ 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 $Fe_3O(OAc)_6(Py)_3$ to give the corresponding amines in good yields.

Oxo-centered triiron carboxylate complexes of the formula $[Fe_3O(OCOR)_6L_3]^{n+}$ (L=neutral ligand, n=0 or 1) have been recently attracted considerable attention, since they exhibit interesting physical properties$^{1)}$ 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 $[Fe^{III}{}_2Fe^{II}O(OAc)_6(Py)_3]$ (**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.

$$ArNO_2 + 6\ HOCH_2CH_2SH \xrightarrow{[Fe_3O(OAc)_6(Py)_3]} ArNH_2 + 3\ (HOCH_2CH_2S\text{-})_2 + 2\ H_2O$$

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-hydroxyethyldisulfide (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 $[Fe^{III}{}_2M^{II}O(OAc)_6(Py)_3]$ (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 Fe≃Mn>Ni>Co. $[Fe^{III}{}_3O(OAc)_6(Py)_3]ClO_4$ 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)]
$[Fe^{III}{}_2Fe^{II}O(OAc)_6(Py)_3]$	97	
$[Fe^{III}{}_2Mn^{II}O(OAc)_6(Py)_3]$	99	
$[Fe^{III}{}_2Co^{II}O(OAc)_6(Py)_3]$	38	57
$[Fe^{III}{}_2Ni^{II}O(OAc)_6(Py)_3]$	63	30
$[Fe^{III}{}_3O(OAc)_6(Py)_3]ClO_4$	96	
$[Fe(Salen)]_2O$ c)	54	45
$[Fe(TPP)]_2O$ d)	7	91
$[Fe(TPP)]OAc$ e)	28	70
$FeCl_2 \cdot 4H_2O$	11	88
$FeSO_4 \cdot 7H_2O$	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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6) The relevant reduction systems Fe^{II}-dihydrolipoamide[8)] and $[Fe_4S_4(SPh)_4]^{2-}$-PhSH[9,10)] have been reported.
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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