The Reduction of Enamines and the Reductive Alkylation of *sec*-Amines with Potassium Hydridotetracarbonylferrate

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Enamines have been recognized to have elegant and broad utility in organic synthesis.[1] On the other hand, little attention has been paid to the reactions of enamines with organotransition metal complexes. The present communication will deal with the reaction of enamines with potassium hydridotetracarbonylferrate, $KHFe(CO)_4$[2] (I), under carbon monoxide.

We have found that enamines react with the alcoholic ferrate (I) at 30°C, with a rapid absorption of carbon monoxide, to give the corresponding saturated amines.[3] No carbonylated product of the enamines was detected, however. The ferrate (I) also reacts with a binary system, consisting of a *s*-amine and a carbonyl compound, from which an enamine can be prepared, to give a *t*-amine in a fairly good yield.

The results of the typical reactions are shown in Table 1. To 11 mmol of the ferrate (I) in 50 m*l* of ethanol, was added 33 mmol of 1-morpholino-1-cyclohexene at 30°C under one atmosphere of carbon monoxide. Twenty mmol of carbon monoxide was absorbed in 1.5 hr, giving 15 mmol of *N*-cyclohexylmorpholine. The reaction also proceeded under nitrogen, but the yield of the product was lower. The yield of the *N*-cyclohexylmorpholine was improved by the addition of excess potassium hydroxide. 1-Piperidino-1-isobutene was readily reduced to the isobutane derivative. The ferrate (I) reacted with an equimolar mixture of morpholine and cyclohexanone, with a slow absorption of carbon monoxide, to give *N*-cyclohexylmorpholine. Neither morpholine and cyclohexanone, however, reacted separately with the ferrate (I). Pyrrolidine and acetophenone gave *N*-(1-phenylethyl)pyrrolidine. The iminium salt of 1-morphorino-1-cyclohexene, *N*-cyclohexylidenemorpholium perchlorate, also reacted with the ferrate (I) to give *N*-cyclohexylmorpholine.

The facts that iron pentacarbonyl is not effective for this type of reduction of enamines, and that the reductive alkylation of *s*-amines with a potassium hydroxide-carbon monoxide system is very slow, show that the ferrate (I) is essential for this reaction. Hydrogenation catalysts, such as Raney nickel[4] and derivativ of formic acid,[5] are effective for the reductive alkylation of amines, but both reactions require some more drastic reaction conditions than does the present reaction. It is plausible that the reduction of enamines and the reductive alkylation of *s*-amines with the ferrate (I) proceeds *via* iminium salt, which has been shown to be an intermediate in the reduction of enamines by formic acids.[6] Studies of the mechanism of this reaction and some of the extension fields of this system will be reported in more detail in the near future.

Table 1. The reduction of enamines and reductive alkylation of amines by $KHFe(CO)_4$[a]

Exp. No.	Reagent[b]	Reaction time, hr	CO absorbed	Max. Rate of CO absorption	Product	Yield
1	1-Morpholino-1-cyclohexene	1.5	1.8[c]	13[d]	*N*-Cyclohexylmorpholine	1.4[c]
2	1-Morpholino-1-cyclohexene	1.5	—[e]	—	*N*-Cyclohexylmorpholine	0.9
3[f]	1-Morpholino-1-cyclohexene	5.0	2.0	10	*N*-Cyclohexylmorpholine	2.4
4	1-Piperidino-1-isobutene	48	1.9	0.8	*N*-Isobutylpiperidine	1.5
5	Morpholine-Cyclohexanone	48	1.7	1.0	*N*-Cyclohexylmorpholine	1.4
6	Pyrrolidine-Acetophenone	48	1.5	1.0	*N*-(1-Phenylethyl)pyrrolidine	1.1

a) $KHFe(CO)_4$ 11 mmol in 50 m*l* ethanol, at 30°C.
b) 3.0 mol/mol-$KHFe(CO)_4$ of reagent was used.
c) mol/mol-$KHFe(CO)_4$.
d) m*l*/min.
e) Nitrogen atmosphere.
f) Excess KOH (11 mol) was added.

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[1] For a review of enamines see, for example, A. G. Cook, "Enamines: Synthesis, Structure and Reaction," Marcel Dekker, New York (1969).

[2] $KHFe(CO)_4$ is formed by the following equation.
$Fe(CO)_5+3KOH \rightarrow KHFe(CO)_4+K_2CO_3+H_2O$

[3] The products in each case were identified by IR, NMR, Mass and vpc analysis.

[4] W. S. Emerson, *Organic Reactions*, **4**, 174 (1949).

[5] M. L. Moore *ibid.*, **5**, 301 (1949); P. L. DeBenneville and J. H. Macartney, *J. Amer. Chem. Soc.*, **72**, 3073 (1950).

[6] N. J. Leonald and R. R. Sauers, *J. Amer. Chem. Soc.*, **79**, 6210 (1957).