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Reduction of Nitro and Nitroso Compounds with Tetracarbonylhydridoferrate

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An applicability of potassium tetracarbonylhydridoferrate as a reducing reagent to synthesis of primary amines from a wide variety of nitro and nitroso compounds has been examined. The reaction proceeds vigorously and exothermally at room temperature to give the corresponding amines in excellent yields. For nitroaryls, some substituents have interfering effect on the formation of amines. *o*-Nitrocinnamic aldehyde gives quinoline.

The reduction of nitro compounds using carbon monoxide, hydrogen, and/or metal carbonyls, and their derivatives has long been of interest. Transition metal carbonyls ($Fe(CO)_5$, $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Co_2(CO)_8$, $[Rh(CO)_2Cl]_2$, $Ni(CO)_4$, and Cu compounds) and their derivatives have been used as reducing catalysts or reagents.[1–12] These compounds have different activities for the reduction of nitro compounds which are converted into a variety of products with groups such as $-NO$, $-N{=}N-$, $-NH_2$, $-NCO$, $>NC(=O)N<$, and $>NOH$. Carbonylferrates, $[Fe(CO)_4]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$, are active for the formation of primary amines from nitro compounds.[1,11] Although tetracarbonylhydridoferrate among the metal carbonyls and their derivatives appears to be effective for the reduction of nitro compounds under mildest conditions, detailed reactivity of this reagent has not been clear.

The present study deals in some detail with the applicability of potassium tetracarbonylhydridoferrate to synthesis of primary amines from nitro and nitroso compounds, mainly substituted nitrobenzenes.

Experimental

Potassium tetracarbonylhydridoferrate was prepared according to the method described in a previous paper:[13] 1.8—3.7 mmol of the ferrate was used in each run. Iron pentacarbonyl, nitrobenzenes, and the other compounds employed were all commercial products.

Reaction Procedure. To the alcoholic ferrate, a certain amount of nitrobenzene or related compounds were stirred in at room temperature under argon or carbon monoxide. After a certain reaction time the reaction mixture was submitted to analysis.

Analytical Procedure. Aniline, cyclohexylamine, and quinoline were analyzed by glpc using internal standards: a column (0.3 cmϕ, 3 m) packed with 10% Versamid on Neopak 60—80 mesh. Other reaction products were isolated as amines or their salts and identified by means of infrared spectra which were recorded on a 215 Hitachi grating spectrophotometer. The products were isolated by evaporating a filtered solution exposed to air for about two days to dryness. For example, the filtered reaction mixture of *o*-nitrobiphenyl (0.95 g, 1.4 mol/mol-$KHFe(CO)_4$) was concentrated to *ca.* 2 ml, IR spectra of which had bands characteristic of *o*-aminobiphenyl, and then the solution was treated with hydrochloric acid and evaporated to dryness to give a white solid, 1.05 g (140%), IR spectra of which had bands characteristic of *o*-aminobiphenyl hydrochloride. *m*-Nitroaniline (0.70 g) gave 1,3-diaminobenzene dihydrochloride as an orange solid, 0.61 g (94%). *o*-Nitrocinnamic acid (1.0 g) gave *o*-aminocinnamic acid as a pale yellow solid, 0.45 g (65%). Carbon dioxide produced in the reaction was volumetrically determined.

Results and Discussion

The ferrate reacted with nitrobenzene to give aniline selectively. The reaction proceeded vigorously and exothermally at room temperature with an evolution of carbon dioxide (about 0.5 mol/mol-$KHFe(CO)_4$) and appeared to complete in several minutes with rapid color change from pale yellow to brown. The results are summarized in Table 1.

TABLE 1. REDUCTION OF NITROBENZENE AND RELATED COMPOUNDS WITH FERRATE[a)]

Substrate[b)]		Reaction time hr	Aniline[c)] %
Nitrobenzene	1.6	0.5	160
Nitrobenzene	2.5	0.5	180
Nitrobenzene	4.0	0.5	180
Nitrosobenzene	4.0	0.5	210
Azobenzene	2.0	10	260
Nitrocyclohexane	2.0	1.5	140[d)]

a) Room temperature under argon. b) mol/mol-$KHFe(CO)_4$. c) Based on an amount of the ferrate used. d) Cyclohexylamine.

The reducing power of one mol of the ferrate corresponds to *ca.* 1.8 mol of nitrobenzene which is selectively converted to an equimolar aniline. At this time about 2.0 mol/mol-$KHFe(CO)_4$ of carbonate, $KHCO_3$, are produced and the ferrate is oxidized to di- or trivalent. This consideration is supported by the fact that nitromethane oxidizes the ferrate in alcohol to ferric hydroxide in 12 hr.[14] Ethanol and water, and the hydrido species are hydrogen sources in this reaction but a mechanism of the hydrogen transfer is not clear.

The reaction proceeds without an absorption of carbon monoxide under carbon monoxide and is not affected by reaction atmospheres, argon and carbon monoxide. On the other hand, the reduction of olefin oxides, isoprene, and enamines with the ferrate is highly affected by the carbon monoxide atmosphere:[15] the reaction is generally accelerated under carbon monoxide with an absorption of the gas and the ferrate in the course of the reaction is converted to polynuclear ferrates, $[Fe_2(CO)_8]^{2-}$ and $[Fe_3(CO)_{11}]^{2-}$, and finally to iron pentacarbonyl. In the reduction of nitrobenzene with the ferrate, nitrobenzene acts as a powerful oxidizing agent and then the ferrate is converted finally to higher valent states inactive to carbon monoxide.

The ferrate had also high reactivity for nitrosobenzene and moderate one for azobenzene. From these, aniline was obtained in excellent yields. Nitrocyclohexane reacted more slowly than nitrobenzene.

Although the reaction is not catalytic, this reagent appears to have a wide applicability to the reduction of nitro and nitroso compounds to primary amines.

TABLE 2. REDUCTION OF SUBSTITUTED NITROBENZENES WITH FERRATE[a)]

Substituted nitrobenzene	Substituted aniline (%)	Substituted nitrobenzene	Substituted aniline (%)
o-Cl	125	*o*-OH	Black solid
m-Cl	105	*m*-OH	85
p-Cl	105	*p*-OH	63
o-CH_3	120	*o*-OCH_3	85
m-CH_3	125	*o*-NH_2	Black solid
p-CH_3	120	*m*-NH_2	95
o-C_6H_5	140	*p*-NH_2	Black solid
o-COOH[b)]	70	*o*-NO_2[c)]	*o*-NH_2 10
m-COOH[b)]	60	*m*-NO_2[c)]	*m*-NH_2 45
p-COOH[b)]	30	*p*-NO_2[c)]	Black solid

a) Room temperature under argon for 30 min. Nitrobenzenes, 1.4 mol/mol-$KHFe(CO)_4$. Dinitrobenzenes, 0.7 mol/mol-$KHFe(CO)_4$. b) $K_2Fe(CO)_4$ was used. c) The ferrate was enough for the reduction of two nitro groups.

The results of the reduction of substituted nitrobenzenes are listed in Table 2. Nitrobenzenes having a variety of functional groups were readily reduced to the corresponding amines. Conditions were not optimized for these compounds. *o*-Nitrobiphenyl gave *o*-aminobiphenyl, but carbazole, which is taken as evidence for nitrene intermediate,[4,10)] was not obtained. Some functional groups can block the formation of amines and positions of the substituents in a benzene ring have a remarkable effect on the reduction. Nitrobenzenes with groups, *o*-OH, *o*-NH_2, *o*-NO_2, and *p*-NO_2 gave intractable black solids, some of which seem to be iron carbonyl-amine complexes,[16)] although further analysis of the solids was not done. These groups, however, have no interfering effect on the formation of amines when located at the *meta* position. Such substituents as –Cl, –CH_3, and –COOH have no interfering effect.

α-Nitronaphthalene and *o*-nitroacetophenone were reduced to the corresponding amines. The ferrate selectively attacked the more reactive nitro group of *o*-nitrocinnamic acid and the olefinic group remained unchanged when an amount of the ferrate used was enough only for the reduction of the nitro group. *o*-Nitrocinnamic aldehyde gave quinoline in an excellent yield, which appears to be derived *via* *o*-aminocinnamaldehyde by an intramolecular condensation.

An *N*-nitroso group had a poor reactivity for the ferrate. *N*-Nitrosodiphenylamine slowly reacted with the ferrate to give diphenylamine which seemed to be derived *via* *N*,*N*-diphenylhydrazine by a N–N bond cleavage. *N*-Nitrosodicyclohexylamine was recovered unchanged under the condition used. ω-Nitrostyrene had a high reactivity for the ferrate but gave an intractable, tarry material.

References

1) German Patent 441179 (1925).

2) S. Murahashi and S. Horiie, This Bulletin, **33**, 78 (1960).

3) G. D. Buckey and N. H. Ray, *J. Chem. Soc.*, **1949**, 1154.

4) J. E. Kmiecik, *J. Org. Chem.*, **30**, 2014 (1965).

5) E. K. von Gustorf, M. C. Henry, R. E. Sacher, and C. DiPietro, *Z. Naturforsch.*, **21b**, 1152 (1966).

6) Brit. Patent (*Chem. Abstr.*, **64**, 11126h (1966)).

7) W. B. Hardy and R. P. Bennett, *Tetrahedron Lett.*, **1967**, 961.

8) T. Kajimoto and J. Tsuji, This Bulletin, **42**, 827 (1969).

9) F. L'Eplattenier, P. Matthys, and F. Calderazzo, *Inorg. Chem.*, **9**, 342 (1970).

10) H. Alper and J. T. Edward, *Can. J. Chem.*, **48**, 1543 (1970).

11) J. M. Landesberg, L. Katz, and C. Olsen, *J. Org. Chem.*, **37**, 930 (1970), and references cited therein.

12) J. F. Knifton, *ibid.*, **38**, 3296 (1973).

13) Y. Takegami, Y. Watanabe, H. Masada, and I. Kanaya, This Bulletin, **40**, 1456 (1967).

14) J. C. Case and M. C. Whiting, *J. Chem. Soc.*, **1960**, 4632.

15) Y. Takegami, Y. Watanabe, T. Mitsudo, I. Kanaya, and H. Masada, This Bulletin, **41**, 158 (1968); Y. Takegami, Y. Watanabe, T. Mitsudo, and H. Masada, *ibid.*, **42**, 202 (1969); T. Mitsudo, Ph. D. Thesis, Kyoto University (1972).

16) A. J. Carty, *Organomet. Chem. Rev.* A, **7**, 191 (1972), and references cited therein.