HIGHLY SELECTIVE REDUCING AGENTS. REDUCTION OF NITROBENZENE TO ANILINE IN THE PRESENCE OF ALDEHYDES, ALKYL HALIDES, AND ACID HALIDES.

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Summary. Although the anionic hydride $[HFe(CO)_{,j}]$ is capable of reducing ketones and aldehydes under acidic conditions, it also selectively reduces nitrobenzene to aniline, even in the presence of benzaldehyde, benzyl chloride, or benzoyl chloride.

The chemistry of the anionic, carbonyl-containing, transition metal hydrides¹ has been richly developed, and these materials are finding application as highly selective reducing agents,² and as deuterium transfer reagents.^{2a} The reactions^{1,3} of hydrides of the type $[HM(CO)_xL_y]^-$ (where L = CO, PR₃, P(OR)₃, etc. and M is any of a number of transition metals) are mechanistically diverse. Thus it is possible to select a particular reducing agent based on a known tendency to react via hydride-based nucleophilicity (e.g. cis-[HW(CO)₄PR₃]⁻), metal-based nucleophilicity (e.g. [HFe(CO)₃PR₃]⁻), or single electron transfer (i.e. radical) pathways (e.g. [C₅H₅V(CO)₃H]⁻ and [HCr(CO)₅]⁻). Because [HFe(CO)₄]⁻ is among the least hydridic (i.e. the poorest hydride-based) nucleophiles of the anionic transition metal hydrides,^{2d} we expected it to display the greatest selectivity as a reducing agent for substrates requiring electron transfer reduction.

Although a number of reports⁴ of the use of $[HFe(CO)_4]^-$ as a reducing agent have appeared, these have largely been studies in which the reducing agent has been generated in situ by the action of excess strong base on Fe(CO)₅. There has, therefore, been some ambiguity about the identity of the active reducing agent, since the hydride must be in equilibrium with the dianion, as shown in equations (1) and (2).

$$Fe(CO)_{5} + OH^{-} \rightarrow CO_{2} + [HFe(CO)_{4}]^{-}$$
(1)
$$[HFe(CO)_{4}]^{-} + OH^{-} \neq [Fe(CO)_{4}]^{2^{-}} + H_{2}O$$
(2)

In the present study, a salt of $[\mathrm{HFe(CO)}_4]^-$ has been employed under acidic conditions, thus extending the useful pH range of the reagent.

The data of the Table were obtained by using gc techniques, comparing the amount of a

given product against a gravimetric standard. The solvents were freshly distilled under argon prior to use, and standard Schlenk techniques were employed to protect the reactions from the atmosphere. The hydride reagent was prepared as the

bis(triphenylphosphine)iminium (PPN⁺) salt, according to the published procedure.⁵ The organometallic product of the reactions was the red trimer hydride, $[HFe_3(CO)_{11}]^{-}$, and ketones and aldehydes are reduced according to the stoichiometry shown in equation (3).

$$3[\text{HFe}(\text{CO})_4] + 2\text{H}^+ + 2\text{R}^1\text{R}^2\text{C=O} \rightarrow 2\text{R}^1\text{R}^2\text{CHOH} + [\text{HFe}_3(\text{CO})_{11}]^- (3)$$

The mole ratio of hydride reactant to Brønsted acid to organic substrate was made to be 3/3/2 (thereby providing a slight mole excess of acid), except where noted in the Table and in cases where a ten-fold excess of $[HFe(CO)_4]^{-1}$ and of Brønsted acid was employed in order to demonstrate the profound selectivity of the reagent for reduction of nitrobenzene.

The reduction of aldehydes or ketones required reflux temperatures, and strong Brønsted acids. No reduction of any of the aldehydes or ketones listed in the Table was observed using methanol as the solvent. Solvent mixtures such as THF/methanol or THF/H₂O were found to give lower yields of reduced organic product than was obtained using THF alone as the solvent. Trifluoroacetic acid gave better yields than did weaker Brønsted acids such as PhOH or CH_2CO_2H .

The efficient reduction to aniline of nitrobenzene alone was accomplished in high yield at room temperature, within 24 hr., by the use of a stoichiometric excess of $[HFe(CO)_4]^-$ and trifluoroacetic acid, in THF solution. The optimum mole ratios of the reactants $[HFe(CO)_4]^-$, trifluoroacetic acid, and nitrobenzene was found to be 5:4:1, respectively. In reactions in which a deficiency of $[HFe(CO)_4]^-$ was employed, some reduction of nitrobenzene to aniline still occurred, and the red trimer hydride $[HFe_3(CO)_{11}]^-$ was formed in concomitant amounts. In cases where infrared spectroscopy indicated that all of the $[HFe(CO)_4]^-$ had been consumed, no further reduction occurred, indicating that the trimer hydride was not the active reducing agent, as has been previously noted.¹

When nitrobenzene was co-dissolved with benzaldehyde, benzyl chloride, or benzoyl chloride, and when a ten-fold excess of $[HFe(CO)_4]^{-1}$ was used along with excess trifluoroacetic acid, the exclusive reduction product in THF, at 25 °C, was aniline, in better than 98 % yield. There was observed to be no reduction of benzaldehyde, benzyl chloride, or benzoyl chloride in these various competition experiments, after 30 hr. The starting amounts of the latter three materials were recovered unchanged after complete reduction of nitrobenzene had been accomplished. Thus although $[HFe(CO)_4]^{-1}$ can be made to reduce aldehydes, ketones, and acid halides, ⁶ we can report here that at room temperature,

in THF solvent, with trifluoroacetic acid, $[\mathrm{HFe(CO)}_4]^{-1}$ is an efficient and selective reducing agent for nitrobenzene, giving aniline exclusively, even in the presence of aldehydes, alkyl halides, or acid halides.

Reactant	Mole Ratios Employed ^a	Temp. °C	Time hr	Product	Solvent	% Yield ^b
						7.0
сн ₃ сн ₂ сно	3/3/2	reflux	2	снзсн2сн2он	THF	70
PhCHO	3/3/2	reflux	24	рьсн ₂ он	THF	75
					THF/MeOH	20
					MeOH	0
2-heptanone	3/3/2	reflux	24	2-heptanol	THF	50
				•	THF/MeOH	20
					MeOH	0
cyclohexanone	3/3/2	reflux	3	cyclohexanol	THF	70
cyclopentanone	3/3/2	reflux	10	cvclopentanol	THF	10
-,	0,0,1			-,		
PhNO2	5/4/1	25	24	PhNH ₂	THF	98
						- C
PhCH ₂ CI	5/4/1	25	24	PhCH ₃	THF	0
PhC(0)C1	5/4/1	25	24	PhCHO	THF	0 ^c
PhC(0)C1	5/4/1	25	24	РҺСН ₂ ОН	THF	0 ^c

Table. Yields of Reduced Organic Products after Reaction with [HFe(CO)₄] and Trifluoroacetic Acid

^a The mole ratio of [HFe(CO)₄] , CF_3CO_2H , and organic substrate, in that order.

^b Determined by gas chromatography.

 $^{\mbox{c}}$ In the presence of, and through-out the reduction of, nitrobenzene.

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