

Reduction of Aromatic Nitro-compounds to Amines with Sodium Borohydride-Copper(II) Acetylacetonate

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The reduction of aromatic nitro-compounds by NaBH_4 in ethanol in the presence of various transition metal acetylacetonates has been investigated. Copper(II) acetylacetonate was found to be the most effective catalyst for reduction to the corresponding amines. This reaction appears to proceed through a hydride metal complex.

AROMATIC nitro-compounds are normally not reduced by sodium borohydride in aqueous or alcoholic solution. Recently, however, there have been a number of reports of the catalysis by transition metal complexes of the reduction of nitroarenes by borohydride.¹⁻⁷ In this paper, we describe a simple and efficient reduction of aromatic nitro-compounds to the corresponding amines by sodium borohydride in the presence of copper(II) acetylacetonate (Table 1).

The nitroarene (0.01 mol), $\text{Cu}(\text{acac})_2$ (260 mg), and sodium borohydride (0.03 mol) in ethanol were stirred at 30 °C for 2–4 h to afford the corresponding amine in 80–90% yield (of isolated material). The yields were generally superior to those reportedly obtained by other methods. For comparison, we examined the reduction of 1-chloro-4-nitrobenzene with sodium borohydride in the presence of $\text{Ni}(\text{acac})_2$, $\text{Co}(\text{acac})_2$, and $\text{Fe}(\text{acac})_3$. The results (Table 2) show that $\text{Cu}(\text{acac})_2$ is the most effective catalyst for reduction to amines. It is conceivable that the conditions for reduction catalysed by

$\text{Ni}(\text{acac})_2$ may be modified to give the azoxy-compound in better yields.

The electrochemical reduction of nitrobenzene is known⁸ to proceed *via* intermediates such as nitrosobenzene, phenylhydroxylamine, azoxybenzene, azobenzene, and hydrazobenzene. In order to shed light on the borohydride reduction path, we examined the reaction of these compounds with sodium borohydride in the presence of $\text{Cu}(\text{acac})_2$; the results are summarized in Table 3.

TABLE 3

Reductions of 1-chloro-4-nitrobenzene, 4,4'-dichloroazoxybenzene, 4,4'-dichloroazobenzene, and *N*-(4-chlorophenyl)hydroxylamine at 30 °C for 2 h

Substrate	Products (%) *		
	Azoxy	Azo	Amine
1-Chloro-4-nitrobenzene			90
4,4'-Dichloroazoxybenzene	50	5	30
4,4'-Dichloroazobenzene		50	30
<i>N</i> -(4-Chlorophenyl)hydroxylamine			90

* Yields of isolated material.

TABLE 1

Reduction of aromatic nitro-compounds in the presence of $\text{Cu}(\text{acac})_2$

R in $\text{RC}_6\text{H}_4\text{NO}_2$	Reaction time (h)	% Yield * of $\text{RC}_6\text{H}_4\text{NH}_2$
H	2	80
4-Cl	2	90
3-Cl	2	80
2-Cl	2	80
4-Me	4	80
3-Me	2	80
2-Me	2	80
4-OMe	4	90
3-OMe	2	80
2-OMe	2	90

* Of isolated product.

TABLE 2

Reduction of 1-chloro-4-nitrobenzene with $\text{M}(\text{acac})_2\text{-NaBH}_4$

M	Reaction temp. (°C)	Reaction time (h)	Product (%) *			
			Azoxy	Azo	Amine	Nitro
Ni ^{II}	30	4	30		5	35
	40	4	35	Trace	5	25
	60	4	30	5	10	Trace
Co ^{II}	30	4	35		5	45
Fe ^{III}	30	4			10	70

* Yields of isolated material.

The excellent yield of the amine from *N*-(4-chlorophenyl)hydroxylamine and the sluggish formation of the amine from the azo- and azoxy-compounds suggest that the reduction might follow the simple pathway nitrobenzene \rightarrow nitrosobenzene \rightarrow phenylhydroxylamine \rightarrow aniline, and that condensation intermediates, such as azoxy- and azo-benzenes, are not likely to be precursors.

Although the detailed mechanism of the reaction is yet to be clarified, it seems likely that the reduction occurs through formation of an initial hydride metal complex. Under similar conditions $\text{Cu}(\text{acac})_2$ reacted with sodium borohydride readily to form a pale brown solution containing a small amount of brown powder. Exposure of this solution to the air did not regenerate $\text{Cu}(\text{acac})_2$. Although the compound responsible for reduction is unclear, it is believed that a copper(I) complex might act as the reducing species.

EXPERIMENTAL

Typical Procedure.—To a suspension of copper(II) acetylacetonate (0.002 mol) in propan-2-ol (20 ml) a solution of sodium borohydride (0.01 mol) in ethanol was

added with stirring under nitrogen at room temperature. To this solution was added the nitro-compound (0.01 mol) in propan-2-ol, followed by sodium borohydride (0.02 mol) in ethanol at 30 °C. The mixture was stirred for 2—4 h at 30 °C. After cooling, water (50 ml) was added, and the solvent was removed under reduced pressure. The residue was extracted with chloroform and the products were analysed by a method similar to those described previously. Reductions of phenylhydroxylamine and azoxy- and azo-compounds were carried out similarly; the residues were then chromatographed on silica gel. The products were identified by i.r. and n.m.r. spectral measurements.

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