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REDUCTION OF AZOBENZENE AND BENZYLIDENEANILINE BY THE COMBINED USE OF COPPER AND N,N-DIETHYLDITHIOCARBAMIC ACID

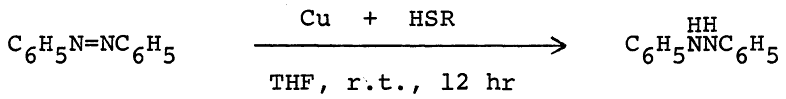
Toshio SATO, Tan INOUE, and Teruaki MUKAIYAMA*
Laboratory of Organic Chemistry, Tokyo Institute of Technology
Ookayama, Meguro-ku, Tokyo 152

Azobenzene or benzylideneaniline was reduced by the combined use of copper and N,N-diethyldithiocarbamic acid to afford hydrazobenzene or 1,2-dianilino-1,2-diphenylethane in good yield, respectively.

Copper is effectively used for the reduction of halides as seen in the Ullmann reaction[1)] of aromatic halides. However, copper is not suitable for the reduction of other hetero atom (N,O,etc.) containing compounds because of its low oxidation potentials (Cu^0/Cu^{2+}, -0.337V; Cu^0/Cu^+, -0.521V).[2)]

In the present investigation, the reduction of nitrogen-nitrogen and nitrogen-carbon double bond such as azobenzene and benzylideneaniline was attempted by the combined use of copper and thiol since sulfur[3)] and nitrogen atoms[4)] coordinate strongly towards both copper and cupric ion.

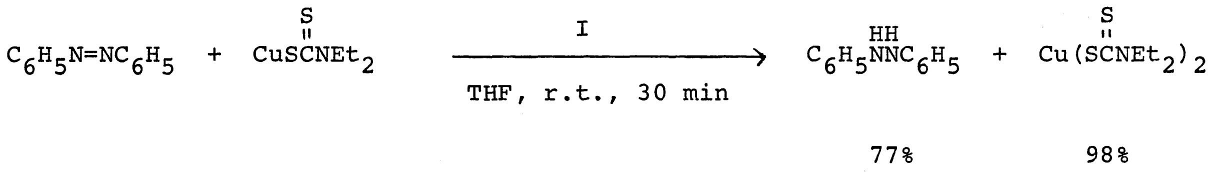
When azobenzene (0.455 g, 2.5 mmol) was treated with copper[5)] and o-aminobenzenethiol (0.69 g, 5.5 mmol) or with copper and N,N-diethyldithiocarbamic acid (I)(0.82 g, 5.5 mmol) in 25 ml of THF at room temperature for 12 hr, hydrazobenzene was obtained in 76 or 66% yield, respectively.



$$C_6H_5N{=}NC_6H_5 \xrightarrow[\text{THF, r.t., 12 hr}]{\text{Cu + HSR}} C_6H_5\overset{H}{N}\overset{H}{N}C_6H_5$$

On the other hand, hydrazobenzene could not be obtained when ethanedithiol, cysteamine, or 2-mercaptoethanol was employed as thiol in the above experiment. The effectiveness of I for the reduction seems to depend on its characteristic affinities towards cupric ion.[6)]

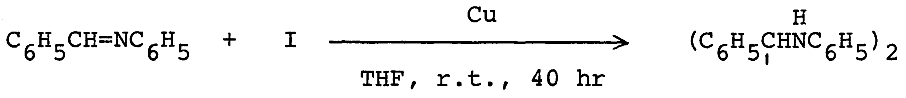
Further, azobenzene was found to be reduced rapidly with cuprous N,N-diethyldithiocarbamate[7)] and I to afford hydrazobenzene in 77% yield.



$$C_6H_5N{=}NC_6H_5 + CuS\overset{\overset{S}{\|}}{C}NEt_2 \xrightarrow[\text{THF, r.t., 30 min}]{\text{I}} C_6H_5\overset{HH}{NN}C_6H_5 + Cu(S\overset{\overset{S}{\|}}{C}NEt_2)_2$$

77% 98%

It was also established that the reductive coupling of benzylideneaniline (IIa) was achieved by utilizing copper and I to afford only 1,2-dianilino-1,2-diphenylethane (IIIa) in good yields as shown in Table I. However, IIIa and considerable amount of N-benzylaniline (IVa) are formed by the reduction of IIa with sodium or lithium in THF at 45-50°C for 22-40 hr after hydrolysis, because of higher oxidation potential of alkali metals.[8)] On the other hand, IVa was obtained in 75% yield when IIa was treated with one mole of benzenethiol and 2,2 moles of both Cu and I.



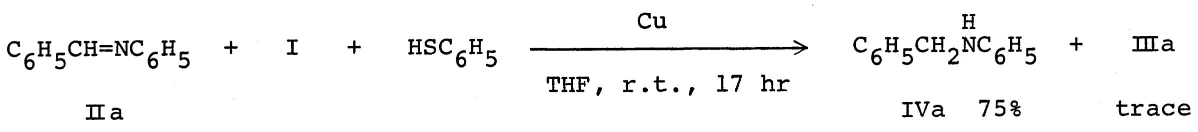
$$C_6H_5CH{=}NC_6H_5 + \text{I} \xrightarrow[\text{THF, r.t., 40 hr}]{\text{Cu}} (C_6H_5\underset{|}{C}H\overset{H}{N}C_6H_5)_2$$

IIa IIIa

Table I. The Reduction of Benzylideneaniline by Cu and I

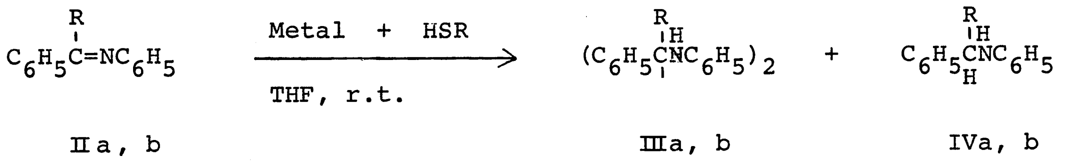
molar ratio			Yield of IIIa[a)], %
IIa	Cu	I	
1.0	1.1	1.1	62
1.0	1.2	2.2	68
1.0	2.2	2.2	71
1.0	2.2	4.4	95

a) The ratio of meso and racemic IIIa was 1 : 1.



$$\underset{IIa}{C_6H_5CH{=}NC_6H_5} + I + HSC_6H_5 \xrightarrow[\text{THF, r.t., 17 hr}]{Cu} \underset{IVa\ 75\%}{C_6H_5CH_2\overset{H}{N}C_6H_5} + \underset{trace}{IIIa}$$

The reduction of acetophenone-anil (IIb) with copper and I resulted in the formation of the corresponding dimeric product (IIIb) in only 16% yield. Instead of copper and I, zinc and O,O-dimethyl dithiophosphate were used for the reduction of II and the results were shown in Table II. The yield of IIIa or IIIb was increased



$$\underset{IIa,\ b}{C_6H_5\overset{R}{C}{=}NC_6H_5} \xrightarrow[\text{THF, r.t.}]{\text{Metal + HSR}} \underset{IIIa,\ b}{(C_6H_5\overset{R}{\underset{|}{C}}\overset{H}{N}C_6H_5)_2} + \underset{IVa,\ b}{C_6H_5\overset{R}{\underset{H}{C}}\overset{H}{N}C_6H_5}$$

(a: R=H, b: R=CH_3)

Table II. The Reduction of II with Metals and Thiols

R	molar ratio					Yields, %	
	II	Cu	Zn	$HS\overset{S}{C}NEt_2$	$HS\overset{S}{P}(OMe)_2$	IIIa[a)]	IV
H[b)]	1.0	1.1		1.1		62	0
H[c)]	1.0		1.1		1.1	81	0
CH_3[b)]	1.0	1.1		1.1		16	4
CH_3[c)]	1.0		1.1		1.1	73	9

a) The ratio of meso and racemic III was 1 : 1.
b) In this case, the reaction time was 40 hr.
c) In this case, the reaction time was 12 hr.

to 81% or 73%, respectively. The results indicate that the combined use of metal with higher oxidation potential and thiol with lower pKa value[9)] is more favorable for this type of reduction.

In conclusion, copper or zinc, in spite of relatively low oxidation potentials, can reduce azobenzene or benzylideneaniline in the presence of N,N-diethyldithiocarbamic acid or O,O-dimethyl dithiophosphate to afford hydrazobenzene or 1,2-dianilino-1,2-diphenylethane in good yield, respectively.

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Hongo, Bunkyo-ku, Tokyo 113

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