Tetrahedron Letters No.30, pp. 3379-3381, 1968. Pergamon Press. Printed in Great Britain.

OXAMIDE FORMATION BY THE REACTION OF COPPER HALIDE, LITHIUM AMIDE AND CARBON MONOXIDE

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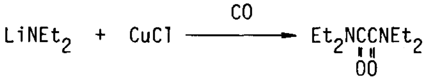
(Received in Japan 15 April 1968; received in UK for publication 29 April 1968)

Although considerable attention has been paid to the insertion reaction of carbon monoxide into transition metal-carbon bond[1], little is known of the reaction of carbon monoxide with metal alcoholate, mercaptide and amide. Recently we reported the reaction of cupric methoxide and carbon monoxide which produced dimethyl carbonate[2]. As to the reaction of metal amides with carbon monoxide, the great majority of works have dealt with alkali metal amides[3].

The present study was undertaken to explore the reaction of carbon monoxide with cuprous amide. In practice, cuprous amide was prepared _in situ_ from lithium amide and cuprous chloride according to a report of Kauffmann et al.[4]. The system of $\mathrm{LiNEt_2}$-CuCl was treated with carbon monoxide. Now, we found that this reaction produced oxamide, e.g.,



$$\mathrm{LiNEt_2} + \mathrm{CuCl} \xrightarrow{\mathrm{CO}} \mathrm{Et_2N}\underset{\mathrm{O}}{\mathrm{C}}\underset{\mathrm{O}}{\mathrm{C}}\mathrm{NEt_2}$$

A typical procedure was as follows. Under nitrogen, cuprous chloride (10 mmoles) was added to an ether solution of lithium N,N-diethylamide (5.0 mmoles) which was prepared from phenyllithium (5.0 mmoles) and diethylamine (5.0 mmoles). This mixture and triethylamine as solvent were added to a 50 ml. stainless steel tube, to which carbon monoxide was compressed up to 60 kg./cm.^{2} at room temperature. The tube was closed and was heated without stirring in an oil bath at 180°C for 19 hrs. Then carbon monoxide was purged off and the reaction mixture was distilled under 1 mmHg at temperature up to 250°C. The distillate was analyzed by g.l.p.c. N,N,N',N'-Tetraethyloxamide was obtained in a yield of 56 %. As a by-product N,N-diethylformamide was formed in a yield of 8 %. Urea was not detected in the reaction mixture. The yields of oxamide under various conditions are shown in the following Table.

TABLE I

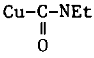
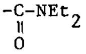
Reaction of Cuprous Chloride, Lithium Amide and Carbon Monoxide[b].

RLi (mmoles)	$HNEt_2$ (mmoles)	CuCl (mmoles)	Et_3N (ml.)	Time (hr.)	Temp. (°C)	Yield of oxamide[a]
^{n}BuLi 10	10	10	7	19	r.t.	2
^{n}BuLi 5	5	5	7	40	70	8
ϕ Li 6.2	6.2	6.4	7	17	120	17
ϕ Li 7.5	7.5	7.7	7	19	180	26
ϕ Li 5	5	10	7	19	180	56
ϕ Li 4.0	4.0	4.0	7	17	210	10

[a] The yields of oxamide are based on diethylamine.

[b] Carbon monoxide pressure is about 60 kg./cm.^{2}.

Reaction temperature and the ratio of cuprous chloride to phenyllithium/diethylamine affect the yields of oxamide. Cupric chloride reacted similarly, but gave poorer yields of oxamide. Cuprous bromide gave a result similar to that of cuprous chloride. As to the effect of solvent on oxamide formation, tetrahydrofuran, 1,2-dimethoxyethane and diethyl ether behaved similarly to triethylamine, but oxamide was not yielded in pyridine. Two reference reactions, cuprous chloride-diethylamine-carbon monoxide and phenyllithium-diethylamine-carbon monoxide, gave only N,N-diethylformamide in low yields.

As to the mechanism of the oxamide formation, it may be assumed that N,N-diethylcarbamoyl copper,  $\text{Cu-}\underset{\underset{\textstyle O}{\|}}{\text{C}}\text{-NEt}_2$, is formed as an unstable intermediate by the insertion of carbon monoxide into Cu-NEt_2 linkage and the coupling of two  $\text{-}\underset{\underset{\textstyle O}{\|}}{\text{C}}\text{-NEt}_2$ groups produces oxamide and metallic copper. The amount of metallic copper in the reaction mixture, however, exceeded that expected from the yield of oxamide. Decomposition of cuprous amide perhaps took place to produce metallic copper. Further works, however, are required to clarify the course of reaction.

This reaction of oxamide formation is interestingly compared with other reactions producing oxamide from carbon monoxide, i.e., palladium catalyzed carbonylation of amine[5] and the reaction of silver acetate, amine and carbon monoxide[6].

In connection with the present study, we carried out the reaction of isolated tetrakis-(diethylamino)titanium, $Ti[N(C_2H_5)_2]_4$, and carbon monoxide and found that oxamide was formed only in a low yield.

REFERENCES

1. M. F. Lappert and B. Prokai, "Advances in Organometallic Chemistry" (Ed. F. G. A. Stone and R. West) Vol. 5, pp 225-319, Academic Press, (1967).
2. T. Saegusa, T. Tsuda, K. Isayama, and K. Nishijima, Tetrahedron Letters, 831 (1968).
3. R. Nast and P. Dilly, Angew. Chem., **79**, 312 (1967); H. Behrens and E. Ruyter, Z. anorg. allg. Chem., **349**, 258 (1967).
4. Th. Kauffmann, J. Albrecht, D. Berger, and J. Legler, Angew. Chem., **79**, 620 (1967).
5. J. Tsuji and N. Iwamoto, Chem. Commun., 380 (1966).
6. T. Saegusa, T. Tsuda, K. Isayama, K. Nishijima, and Y. Isegawa, Tetrahedron Letters, 1341 (1968).