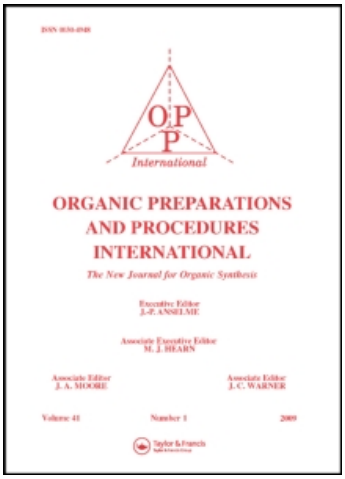

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EFFECT OF METAL IONS IN ORGANIC SYNTHESIS. PART VIII CONVERSION OF ACYLHYDRAZINES AND N-ACYL-N'-TOSYLHYDRAZINES TO AMIDES IN THE PRESENCE OF CUPRIC CHLORIDE

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There was no depression of the mp. upon admixture with an authentic sample of the anhydride.

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EFFECT OF METAL IONS IN ORGANIC SYNTHESIS. PART VIII

CONVERSION OF ACYLHYDRAZINES AND N-ACYL-N'-TOSYLHYDRAZINES TO AMIDES IN THE PRESENCE OF CUPRIC CHLORIDE

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In the general context of the increasing interest in the role of the transition and non-transition metals in organic and biological chemistry,[1]

the conversion of some acylhydrazines and N-acyl-N'tosylhydrazines to carboxylic acids and esters by hydrolysis and alcoholysis in the presence of copper (II) chloride dihydrate was studied.[2]

We now report that the conversion of some acylhydrazines and N-acyl-N'-tosylhydrazines to amides in the presence of copper (II) chloride di-

$$RCONHNHR' + CH_3(CH_2)_2NH_2 \xrightarrow[THF]{CuCl_2} RCONHCH_2CH_2CH_3$$

$$R = Ph,\ PhCH_2,\ PhCH_2CH_2,\ CH_3(CH_2)_{14};\ R' = H,\ Tos$$

hydrate, in contrast to previous investigations,[3] proceeds in good yields under very mild conditions (Table) with inexpensive and easily available reagents.

TABLE. Conversion of Hydrazides to Amides

	Percentage Yield of $RCONHCH_2CH_2CH_3$	
R	R' = Tos	R' = H
Ph	85	55
$PhCH_2$	80	80
$PhCH_2CH_2$	80	70
$CH_3(CH_2)_{14}$	70	70

EXPERIMENTAL

General Procedure.- To a solution of the hydrazide (1 mmol) in tetrahydrofuran (10 ml) was added a solution of copper (II) chloride dihydrate (1.25 mmol) in tetrahydrofuran (10 ml); the mixture was cooled in an ice-bath. To a solution of copper (II) chloride dihydrate (1.25 mmol) in tetrahydrofuran (10 ml) was added a solution of propylamine (10 mmol) in tetrahydrofuran (10 ml); the green solution became violet. It was cooled in an ice-bath and then was slowly added to the hydrazide solution. Initially, the

hydrazide solution remained green and then became violet. The reaction was allowed to proceed for 2 hrs with stirring. The mixture was then concentrated to a small volume under reduced pressure and the residue was extracted with ether (20 ml), 10% aqueous sulfuric acid (3 x 15 ml) and then 10% aqueous sodium hydroxide (3 x 15 ml). The organic phase was washed with water, dried over sodium sulfate and evaporated under reduced pressure to afford the amide in good purity. Further purification was achieved by usual procedures. The isolated products were identified by comparison with authentic specimens, prepared by standard methods.

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ETHYL 3,4-DIHYDROXY-5-METHOXYBENZOATE, AN INTERMEDIATE PRODUCT FOR THE SYNTHESIS OF 3,4-DIHYDROXY-5-METHOXYBENZOIC ACID

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3,4-Dihydroxy-5-methoxybenzoic acid (III) was synthesized by a simple method from methyl gallate.[1]