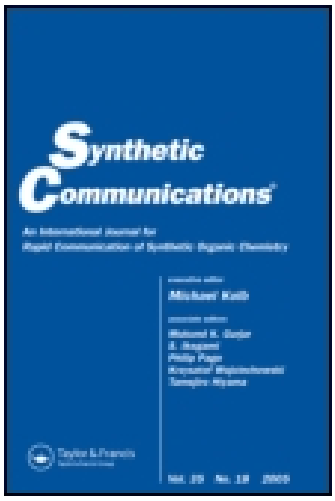

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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Published online: 16 Aug 2006.

To cite this article: K. Mogilaiah, M. Prashanthi & G. Randheer Reddy (2003) An Efficient Oxidation of Acid Hydrazides to N,N′-Diacylhydrazines Using Copper(II) Acetate in Solvent-Free Conditions Under Microwave Irradiation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 33:21, 3741-3745, DOI: 10.1081/SCC-120025183

To link to this article: http://dx.doi.org/10.1081/SCC-120025183

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SYNTHETIC COMMUNICATIONS®
Vol. 33, No. 21, pp. 3741–3745, 2003

An Efficient Oxidation of Acid Hydrazides to *N*,*N*′-Diacylhydrazines Using Copper(II) Acetate in Solvent-Free Conditions Under Microwave Irradiation

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ABSTRACT

A simple and efficient method for solvent free "dry" state transformation of acid hydrazides **1** to corresponding *N*,*N*′-diacylhydrazines **2** using copper(II) acetate under microwave irradiation has been described. The products are obtained in good yields and excellent purities.

There is a growing popularity of using microwave irradiation to carry out solventless reactions and hence become an attractive method for chemical synthesis.[1–4] It involves neat reactants to be exposed to microwave irradiation so as to get greater selectivity and achieve high

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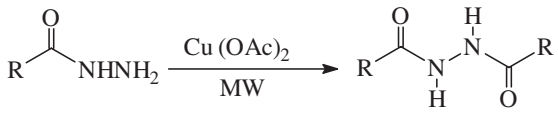
DOI: 10.1081/SCC-120025183 0039-7911 (Print); 1532-2432 (Online)

yields within a short reaction time and with ease in experimentation. Furthermore, the solid state reaction (or solvent-free reactions) has many advantages: reduced pollution, low cost, simplicity in process, and handling. Recently an informative review by Tanaka and Toda[5] clearly points out the superiority of this solvent-free or the use of "dry" reaction conditions in chemical synthesis. Diacylhydrazines are very useful synthons for a variety of bioactive molecules. The oxidative coupling of acid hydrazides is an important method for the formation of diacylhydrazines. Several reagents are documented on the literature to effect this conversion, however these reagents suffer from certain drawbacks such as usage of toxic reagents like LTA, long reaction periods, low yields of the products, use of expensive reagents, and cumbersome work-up procedures.[6–8] Therefore, introduction of new methods and inexpensive reagents for such oxidative dimerizations is still in demand. Copper(II) acetate is an inexpensive and readily available oxidizing agent. In view of this and in continuation of our interest on microwave assisted organic transformations,[9–12] herein we report a simple and efficient method for the conversion of acid hydrazides to *N*,*N*′-diacylhydrazines using copper(II) acetate in solvent-free conditions under microwave irradiation.

Treatment of the acid hydrazides **1** with copper(II) acetate without any solvent under microwave irradiation resulted in the formation of *N*,*N*′-diacylhydrazines **2** in very good yields (Sch. 1). The reaction is clean and efficient. The products were formed in excellent purities in a short reaction time. The high yield transformation did not form any undesirable by-products. The process is environmentally benign. The experimental procedure is very simple.

In a typical case, an equimolar amount of benzhydrazide **1a** and copper(II) acetate were mixed in a conical flask, covered with a funnel and this neat mixture was irradiated in a microwave oven at 700 W. Within 2.5 min the mixture was fused and this liquid on cooling became semi-solid. After usual work-up *N*,*N*′-dibenzoylhydrazine **2a** was obtained in 82% yield.



1 **2**

Scheme 1.

The generality of this facile transformation was established by treating other acid hydrazides **1b–j** with copper(II) acetate under microwave irradiation to get the corresponding *N*,*N*′-diacylhydrazines **2b–j** in high yields. The results are summarized in Table 1. Thus to the best of our knowledge this is the first report on solid state, microwave assisted oxidative dimerization of acid hydrazides using copper(II) acetate.

A plausible mechanism for the conversion of **1** to **2** is outlined in Sch. 2. The intermediacy of acyldiimide **4** in the oxidative dimerization of acid hydrazides has previously been suggested by others.[13–15]

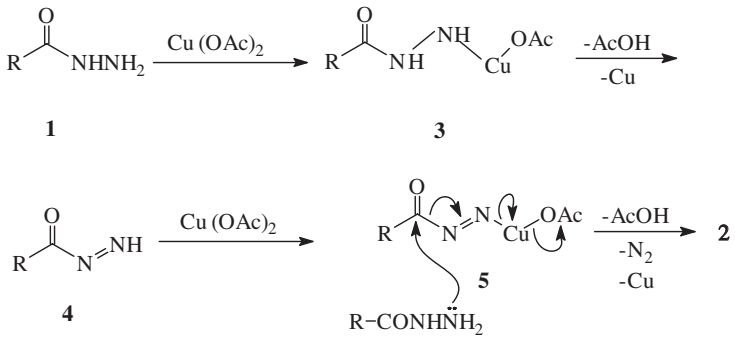
In conclusion, we have described an efficient, rapid, and convenient procedure for the oxidation of acid hydrazides to *N*,*N*′-diacylhydrazines using copper(II) acetate under microwave irradiation in solvent-free conditions. This method has the additional advantages of simple performance, high yields, short reaction times, economic viability, easy work-up, high purity of the products, and minimum environmental impact.

EXPERIMENTAL

Melting points were determined on Cintex melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer spectrum BX series FT-IR spectrophotometer and ^{1}H NMR spectra on a Varian Gemini 200 MHz spectrometer using Me_4Si as internal standard. Analytical TLC was performed on Merck 60F-254 silica gel

Table 1. Microwave assisted oxidation of acid hydrazides **1** to *N*,*N*′-diacylhydrazines **2** using copper(II) acetate.

Product	Ar	Reaction time (min)	Yield (%)	M.p. (°C)	M.p.[Ref.] (°C)
2a	C_6H_5	2.5	82	237–238	238–240[16]
2b	4-$CH_3C_6H_4$	5	86	252–253	253–254[17]
2c	4-$CH_3OC_6H_4$	4	78	227–228	228–228.5[18]
2d	2-ClC_6H_4	6	84	220–221	219–221[7]
2e	4-ClC_6H_4	5	90	291–292	292[18]
2f	2-HOC_6H_4	1	76	296–297	298[19]
2g	2-$NO_2C_6H_4$	5	75	297–298	298[20]
2h	4-$NO_2C_6H_4$	7	80	287–288	291[20]
2i	3-C_5H_4N	4.5	83	223–224	225[20]
2j	4-C_5H_4N	4	85	253–254	253–255[21]



Scheme 2.

plates. Microwave irradiations were carried out in BPL 800 G microwave oven.

General Procedure for the Conversion of Acid Hydrazides 1 to *N,N′*-Diacylhydrazines 2

A mixture of appropriate acid hydrazide **1** (0.01 mol) and copper(II) acetate (0.01 mol) were mixed together without any solvent in a 100 mL conical flask capped with a glass funnel and irradiated in a microwave oven at 700 W for appropriate time (Table 1). After complete conversion as indicated by TLC, to the reaction mixture was added water (50 mL) and conc. HCl (2 mL). The solid separated was filtered and recrystallized from ethanol to afford **2** (Table 1).

ACKNOWLEDGMENT

The authors are thankful to the Director, IICT, Hyderabad for recording ^{1}H NMR spectra.

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