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# Microwave Assisted Deprotection of *N*,*N*-Dimethylhydrazones in Water Using Palladium Chloride–Tin Chloride as Catalyst

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**Summary.** *N*,*N*-Dimethylhydrazones of ketones and aldehydes undergo facile cleavage to the corresponding carbonyl compounds upon exposure to microwaves in water containing a catalytic amount of $PdCl_2$–$SnCl_2$ in high yields.

**Keywords.** Dimethylhydrazones; Deprotection; Palladium; Microwave irradiation.

## Introduction

The deprotection of hydrazones to carbonyl compounds is an important transformation in organic synthesis [1]. In recent years, many reagents compatible with a wide range functionalities have been developed to regenerate carbonyl compounds from the corresponding dialkylhydrazones, thus allowing the use of hydrazones in the total synthesis of complex natural products [2]. Some of the procedures reported earlier for the deprotection of hydrazones involve oxidative cleavage by ozone [3], singlet oxygen [4], $NaIO_4$ [5], or dimethyldioxirane [6] or hydrolytic cleavage by oxalic acid [7], salts [8], or $BF_3 \cdot OEt_2$ [9]. These methods, however, have certain limitations as *e.g.* the use of stoichiometric amounts of reagents and organic solvents, which are often inherently toxic or require tedious work-up procedures. The catalytic method has only been reported using bismuth [10] and palladium [11]. The cleavage of *N*,*N*-dimethylhydrazones using Pd requires long reaction times (24–72 h) and *DMF*–$H_2O$ as solvent.

Microwave enhanced chemical reactions have gained popularity with respect to usual homogeneous and heterogeneous reactions [12]. We report here a facile deprotection of dimethylhydrazones to carbonyl compounds using $PdCl_2$–$SnCl_2$ as the catalyst in water in a process that is accelerated by microwave irradiation.

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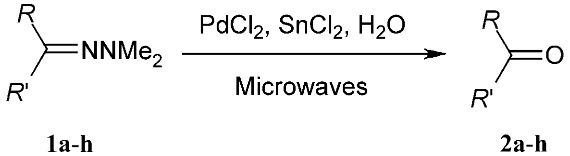
## Results and Discussion

Using $PdCl_2$–$SnCl_2$ under microwave irradiation, various dimethylhydrazones were successfully deprotected to give the corresponding carbonyl compounds (Table 1). The data indicate that deprotection of a variety of dimethylhydrazones readily occurs under these conditions.

When acetophenone *N*,*N*-dimethylhydrazone (**1a**; entry 1) was treated with a catalytic amount of $PdCl_2$–$SnCl_2$ in water under microwave irradiation, acetophenone was obtained in excellent yield. However, when **1a** was treated with $Pd(OAc)_2$ under the same conditions, **2a** was obtained in 83% yield (entry 2). When $SnCl_2$, $PdCl_2$, or both of them were absent, the corresponding ketone was obtained in lower yield (entries 3–5). The cleavage of other acyclic or cyclic *N*,*N*-dimethylhydrazones proceeded easily with good yields (entries 6–12). Octanal *N*,*N*-dimethylhydrazone (**1h**; entry 12) afforded octanal in 88% yield when reacted employing 0.03 equiv. of this catalyst system.

In conclusion, the present methodology offers an efficient, fast, and environmentally friendly procedure for the deprotection of *N*,*N*-dimethylhydrazones to the corresponding carbonyl compounds. A particularly noteworthy advantage of this method is the dramatically shortened reaction time (from hours to seconds) without the need to use organic solvents.

**Table 1.** Regeneration of carbonyl compounds from *N*,*N*-dimethylhydrazones with $PdCl_2$–$SnCl_2$ under microwave irradiation



| Entry | Hydrazone | | | Conditions | Yield/%[a] |
|---|---|---|---|---|---|
| | | *R* | *R'* | | |
| 1 | **1a** | Ph | $CH_3$ | [b] | 98 |
| 2 | **1a** | Ph | $CH_3$ | $Pd(OAc)_2$ instead of $PdCl_2$ | 83 |
| 3 | **1a** | Ph | $CH_3$ | without $SnCl_2$ | 18 |
| 4 | **1a** | Ph | $CH_3$ | without $PdCl_2$ | 32 |
| 5 | **1a** | Ph | $CH_3$ | without $PdCl_2$ and $SnCl_2$ | 10 |
| 6 | **1b** | Ph | $CH_3CH_2$ | [b] | 97 |
| 7 | **1c** | 2-Naphtyl | $CH_3$ | [b] | 79 |
| 8 | **1d** | $PhCH_2CH_2$ | $CH_3$ | [b] | 89 |
| 9 | **1e** | $CH_3(CH_2)_5$ | $CH_3$ | [b] | 88 |
| 10 | **1f** | $CH_2(CH_2)_4CH_2$ | | [b] | 82 |
| 11 | **1g** | $CH_2(CH_2)_3CH_2$ | | [b] | 78 |
| 12 | **1h** | $CH_3(CH_2)_6$ | H | [b] | 88 |

[a] GLC yields; retention times compared with authentic samples; [b] 1 equiv. substrate, 0.03 equiv. $PdCl_2$, 0.03 equiv. $SnCl_2 \cdot 2H_2O$, $2\,cm^3$ $H_2O$

## Experimental

All reactions were carried out in a domestic microwave oven (Moulinex Microchef, 900 W). *N,N*-Dimethylhydrazones **1a–h** were prepared from the corresponding carbonyl compounds according to standard methods [13]. All isolated carbonyl compounds were identified by GLC, IR, and NMR and gave satisfactory results in comparison with authentic samples. GC: Perkin Elmer 8700, FID, He as a carrier gas.

### *General procedure*

A mixture of 1 mmol hydrazone, 0.03 mmol $PdCl_2$, 0.03 mmol $SnCl_2 \cdot 2H_2O$, and 2 $cm^3$ $H_2O$ in a 25 $cm^3$ beaker was irradiated in a microwave oven for 90 s. After irradiation (9 × 10 s, 5 min intervals) and cooling the mixture was extracted with 2 × 20 $cm^3$ ethyl acetate. The organic layer was separated and dried ($Na_2SO_4$). After filtration, the solvent was evaporated, and the residue was analyzed by GC and purified on a short silica gel column (eluent: light petroleum ether:ethyl acetate = 10:1).

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