

# Solvent-free solid-supported recovery of carbonyl compounds from *N,N*-dimethylhydrazones under microwave irradiation

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## Abstract

Efficient conversion of various solid supported *N,N*-dimethylhydrazones into their corresponding ketones was achieved using microwave irradiation and under solvent-free conditions in short time periods.

**Keywords:** Solid support, solvent-free reaction, ketones, hydrazones, microwave irradiation

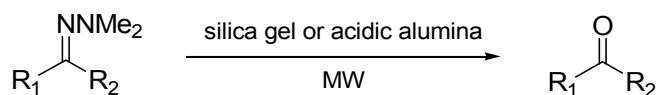
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## Introduction

*N,N*-Dialkylhydrazones are among the most useful equivalents of carbonyl compounds due to their versatility in synthetic organic chemistry avoiding most of the problems and side reactions associated with conventional carbonyl chemistry and allowing smooth construction of C-C and C-X bonds  $\alpha$  to the carbonyl group via electrophilic substitution reactions.<sup>1</sup> Therefore, cleavage of the dialkylhydrazones to liberate the original carbonyl moieties becomes very important.<sup>2</sup> In the last two decades many oxidative,<sup>3</sup> reductive,<sup>4</sup> hydrolytic,<sup>5</sup> and enzymatic<sup>6</sup> procedures have been developed to offer more convenient and efficient procedures for this conversion. Recently, some reports were disclosed for deprotection of dialkylhydrazones involving the use of silica gel solid support in combination with the use of silica chloride,<sup>7</sup> mercuric nitrate,<sup>8</sup> or  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ .<sup>9</sup> However, use of solvents under refluxing conditions, presence of extra additives, and relatively long reaction times strongly indicate the demand to develop more facile, rapid, and additive-free procedures for this transformation.

With increasing global environmental concerns, application of eco-friendly reagents, solid state procedures,<sup>10</sup> solvent-free reactions,<sup>11</sup> and microwave irradiation techniques<sup>12</sup> has increased dramatically in recent years since use of expensive and hazardous organic solvents and reagents can be avoided significantly. In continuation of our interests on solid supported and microwave-promoted reactions,<sup>13</sup> we would like to report here a simple fast microwave-promoted procedure

for efficient additive-free conversion of *N,N*-dialkylhydrazones into their initial ketones using silica gel or acidic alumina as inexpensive convenient heterogeneous catalysts (Scheme 1).



**Scheme 1.** Microwave promoted regeneration of ketones on solid phase.

## Results and Discussion

Table 1 summarizes the results obtained for solid supported deprotection of *N,N*-dialkylhydrazones under microwave-irradiation and solvent-free conditions.

Initially, *N,N*-dimethylhydrazone of 2-octanone adsorbed onto silica gel (or acidic alumina) was subjected to the reaction conditions. Experiments were complete within 4.5 minutes as monitored by TLC showing the disappearance of the starting hydrazone. The  $^1\text{H}$  NMR spectrum of the crude reaction mixture showed complete conversion of the starting material into 2-octanone as the major product in the mixture (entry 1). Bulb to bulb distillation of the crude mixture gave 75% (92%) of the desired product. Control experiments confirmed the combined promoting effect of the solid support and microwave irradiation. When the starting hydrazone was irradiated in a microwave oven without the solid support for several minutes, only formation of small amount of 2-octanone was detected. Alternatively, similar reaction in the absence of microwave irradiation after several hours led to nearly 80% recovery of the starting hydrazone.

The generality of the method was illustrated by subjecting other methyl and aryl hydrazones (entries 2-7), cyclic hydrazones (entries 8-11), and  $\alpha$ - $\beta$ -unsaturated hydrazones (entries 12-14) to the same reaction conditions. Consequently, the corresponding ketones were obtained within 4.5 minutes in 60–78% and 80-98% when silica gel and acidic alumina were used, respectively. The identity of the products was confirmed by the comparison of their physical and spectral data with the reported values.

**Table 1.** Microwave-assisted recovery of carbonyl compounds on solid supports

Entry	Hydrazone	Ketone		Yield (%) <sup>a</sup>	
				silicagel	acidic alumina
1			R = n-C <sub>6</sub> H <sub>11</sub>	75	92
2			R = PhCH <sub>2</sub> CH <sub>2</sub>	62	92
3			R = PhCOCH <sub>2</sub>	64	83
4			R = Ph	65	98
5			R = 2-naphthyl	75	98
6			R = C <sub>2</sub> H <sub>5</sub>	70	90
7			R = Ph	60	85
8			X = CH <sub>2</sub>	71	83
9			X = CH <sub>2</sub> CH <sub>2</sub>	78	97
10			X = S	68	85
11				70	82
12				62	80
13				74	90
14				65	92

<sup>a</sup>isolated yields

## Conclusions

In summary, the microwave-promoted solid-supported conversion of *N,N*-dimethylhydrazones to their respective carbonyl compounds was carried out within few minutes under solvent-free conditions. Higher conversions were observed when acidic alumina was used as the solid support. The environmental safety of the process, high yields of the products, and rapid completion of the reactions are the advantages of this method.

## Experimental Section

**General.** A Moulinex microwave oven (MICRO-CHEF, 900 W at 2450 MHz) was used for irradiation of the reaction mixtures. All reported yields are isolated yields. TLC experiments were carried out on ready-to-use silica gel plates with UV indicator from Aldrich and compounds were visualized by UV fluorescence or by staining with iodine vapor. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrophotometer using KBr disks or as neat samples.  $^1\text{H}$  NMR spectra were recorded on FT-NMR Bruker AC (80 MHz) instruments with  $\text{CDCl}_3$  as solvent and TMS as internal reference. GC-MS spectra were obtained on a Fisons 8000 Trio instrument at ionization potential of 70 eV. *N,N*-dialkylhydrazones were synthesized according to available method.<sup>14</sup> Ketones were purchased from commercial sources and used as received.

**Typical procedure for the recovery of ketones.** A mixture of the hydrazone (5.0 mmol) and silica gel or acidic alumina (4.0 g) was placed in a 25 mL flask and the mixture was irradiated in the microwave oven at high power for 3 x 1.5 minutes with 1 minute intervals. The reaction was monitored by TLC and complete disappearance of the starting material was observed during this period. The mixtures were cooled to room temperature, stirred in ether (20 mL), and filtered through a Celite column. The filtrate was concentrated at reduced pressure and the respective ketone was purified by bulb-to-bulb distillation, if necessary. The  $^1\text{H}$  NMR, IR, and GC-MS spectra of the products were obtained and compared with those reported in the literature.

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