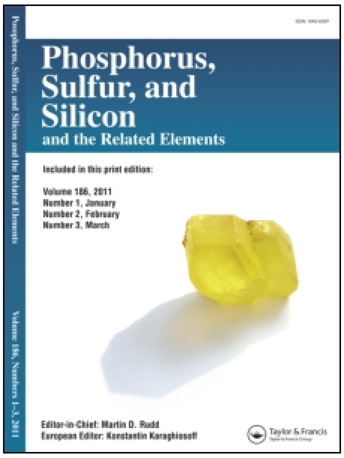

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A Mild and Convenient Method for Conversion of Thioamides to Their Corresponding Amides Using Acidified Wet Silica-Supported Permanganate Under Solvent-Free Conditions

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A Mild and Convenient Method for Conversion of Thioamides to Their Corresponding Amides Using Acidified Wet Silica-Supported Permanganate Under Solvent-Free Conditions

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A mild and efficient method for conversion of thioamides to their corresponding amides is reported. A series of thioamides are transformed to their corresponding carbonyl compounds in good to excellent yields by acidified wet silica-supported permanganate under solid phase conditions.

Keywords Acidified wet silica-supported permanganate; amides; solvent-free; thioamides

INTRODUCTION

The transformation of thioamides to their corresponding amides is a significant reaction in synthetic organic chemistry. Amides are valuable chemical intermediates in some organic reactions; they can be dehydrated to nitriles, hydrolyzed to carboxylic acids, and degraded to amines in Hofmann rearrangement. Since all peptides and proteins are produced from natural α-amino acids, these compounds are very prevalent in nature. One of the available methods for preparation of amides is the chemical transformation of thioamides into their corresponding oxo-derivatives, i.e., amides, is highly valuable for the nucleic thiobases and thionucleosides.[1]

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Thiocarbonyl compounds are specific and beneficial tools for multistep synthetic routes leading to various natural products or biologically active molecules.[2] However, the final step of a total synthesis may involve transformation of a thiocarbonyl group into the corresponding carbonyl group. Various methods and reagents such as *t*-butyl hypochlorite,[3] diaryl selenoxide,[4] dimethyl selenoxide,[5] diaryl telluroxide,[6] benzeneseleninic anhydride,[7] singlet-oxygen,[8] thiophosgene,[9] sodiumperoxide,[10] dimethyl sulfoxide/iodine,[11] *m*-chloroperbenzoic acid,[12] $NOBF_4$,[13] *N*-nitrosamines,[14] soft NO^+ species,[15] trifluoroacetic anhydride,[16] clayfen,[17] *p*-nitrobenzaldehyde/TMSOTf,[18] 2-nitrobenzenesulfonyl chloride/potassium superoxide,[19] manganese dioxide,[20] clayfen or clayan/MW,[21] Caro's acid supported on silica gel,[22] ceric ammonium nitrate,[23] oxone,[24] $(n\text{-BuPPh}_3)_2S_2O_8$,[25] $(n\text{-BuPPh}_3)_2Cr_2O_7$,[26] 3-carboxypyridinium and 2,2′-bipyridinium chlorochromates,[27] and tetrabutylammonium periodate[28] have been reported for the deprotection of thiocarbonyl compounds to their oxygen analogues.

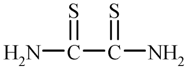
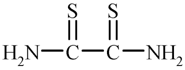
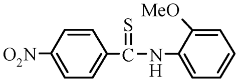
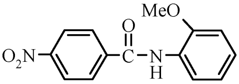
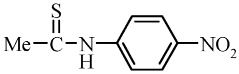
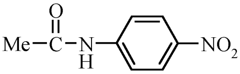
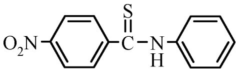
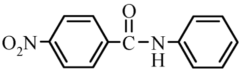
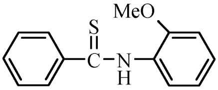
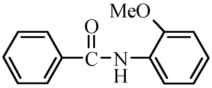
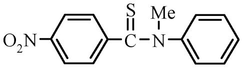
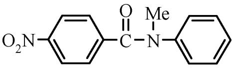
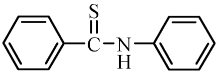
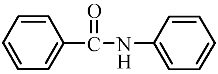
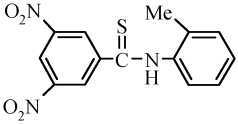
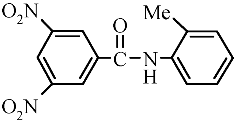
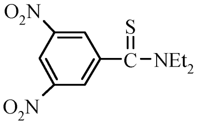
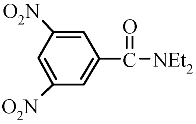
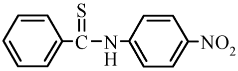
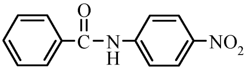
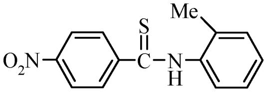
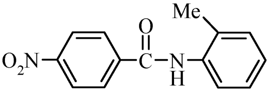
However, some of these methods have certain limitations such as long reaction times,[4–6,19] toxic or expensive reagents,[7,9,13–15] low yields of the products[4,5,19] and tedious procedures.[7,10,15,18] Furthermore, some of these methods are not suitable for deprotection of primary thioamides.

The use of solid supports has become popular due to their characteristic properties such as enhanced reactivity and selectivity, straightforward work-up procedure, milder reaction conditions, and associated ease of manipulation.[29] One of the most striking examples of such a change in chemical reactivity that has been reported to date is with potassium permanganate.[30] The heterogeneous reaction of sulfides, alkenes, unsaturated alcohols, benzylic carbons, and α-sulfinyl oximes and α-sulfinyl hydrazones with potassium permanganate supported on copper sulfate, alumina, or silica gel are different than heterogeneous aqueous reactions.[31,32]

RESULTS AND DISCUSSION

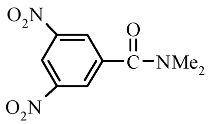
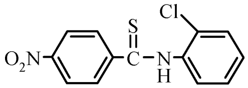
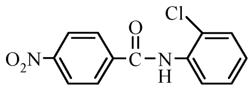
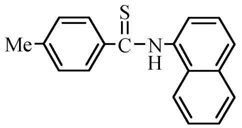
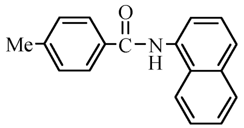
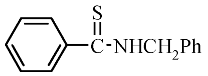
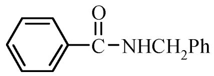
As shown in Table I, a variety of thioamides (primary, secondary, and tertiary) were treated with $KMnO_4$/acidified wet SiO_2 under solid phase conditions at room temperature to afford the corresponding carbonyl compounds in good to excellent yields (Table I, entries 1–15). In the absence of acid, the conversion of thioamides decreased to 5–10%, and in the absence of SiO_2 the thioamides remained intact.

TABLE I Transformation of Thioamide Derivatives to the Corresponding Amides with KMnO$_4$/Acidified Wet SiO$_2$

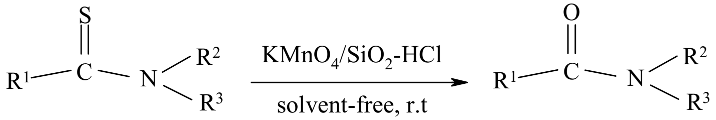
Entry	Thioamides	Amides	Time (min)	Yields (%)	Ref.
1	 $H_2N-\overset{S}{\overset{\|}{C}}-\overset{S}{\overset{\|}{C}}-NH_2$	 $H_2N-\overset{S}{\overset{\|}{C}}-\overset{S}{\overset{\|}{C}}-NH_2$	9	92	[35]
2			7	93	[37]
3			5	96	[35]
4			4	98	[36]
5			16	93	[36]
6			9	96	[37]
7			8	94	[35]
8			4	95	[37]
9			5	94	[37]
10			6	98	[35]
11			5	90	[37]

(Continued on next page)

TABLE I Transformation of Thioamide Derivatives to the Corresponding Amides with $KMnO_4$/Acidified Wet SiO_2 *(Continued)*

Entry	Thioamides	Amides	Time (min)	Yields (%)	Ref.
12			2	97	[37]
13			3	94	[37]
14			6	92	[37]
15			9	93	[35]

Large scale deprotection of some thioamides to their corresponding amides was also investigated in a 20 mmol scale. The results were comparable to those of small scale experiments; therefore, it seems that this methodology is also applicable for operation on large scale desulfurization of thioamides. It was found that in these reactions sulfur is converted to sulfate and replaced by oxygen, which is indicated by addition of a solution of $BaCl_2$.



CONCLUSION

We have developed a mild and convenient procedure for the conversion of thioamides to their carbonyl compounds using $KMnO_4$/acidified wet SiO_2 as a nontoxic and inexpensive reagent under solvent-free conditions. The short reaction times, high product yields, and heterogeneous nature of the reagent are the advantages of this method.

EXPERIMENTAL

All of the products were identified by comparison of their physical and spectral data with those of authentic samples. The starting thioamides were prepared according to described procedures.[33,34]

GENERAL PROCEDURE

Acidified wet silica gel was prepared by shaking silica gel (20 g, 70–230 mesh) with concentrated HCl (6 mL). The reagent was prepared by mixing of $KMnO_4$(2 mmol, 3.23 g) with acidified wet-silica gel (3 g) using a pestle and mortar until a fine, homogeneous, purple powder was obtained. A mixture of thioamides (1 mmol) and $KMnO_4$/ acidified wet SiO_2 (2 mmol, 3.23 g) was ground with a pestle and mortar until TLC showed complete disappearance of thioamides, which required 2–12 min (Table I). Ethylacetate (2 × 10 mL) was added to the reaction mixture, and after vigorous stirring, was filtered through a sintered glass funnel. After evaporation of the solvent and purification by column chromatography on silica gel using ethyl acetate as eluent, the pure amides were obtained in 92–98%.

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