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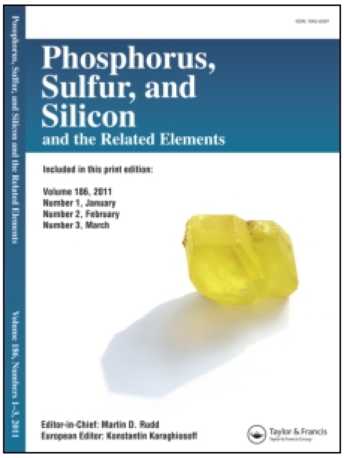

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Acidified, Wet, Silica-Supported Tetrabutylammonium Periodate: A Convenient and Mild Reagent for Conversion of Thioamides to Their Corresponding Amides Under Solvent-Free Conditions

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Acidified, Wet, Silica-Supported Tetrabutylammonium Periodate: A Convenient and Mild Reagent for Conversion of Thioamides to Their Corresponding Amides Under Solvent-Free Conditions

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A series of thioamides are transformed to their corresponding oxo analogues in good to excellent yields with acidified, wet, silica-supported tetrabutylammonium periodate under solvent-free conditions.

Keywords Acidified; wet; silica-supported tetrabutylammonium periodate; oxidations; solid state; solvent-free; thioamides

INTRODUCTION

The production and removal of functional groups is of great importance in the synthesis of polyfunctional organic molecules. The conversion of thiocarbonyl compounds to their oxygen analogues has received considerable attention, not only for the development of innovative synthetic methods but also for their vast potential in medicinal chemistry.[1]

Over the last years, several new oxidizing reagents such as diaryl selenoxide,[2] dimethyl selenoxide,[3] t-butyl hypochlorite,[4] benzeneseleninic anhydride,[5] singlet-oxygen,[6] diaryl telluroxide,[7] thiophosgene,[8] sodium peroxide,[9] dimethyl sulfoxide/iodine,[10] N-nitrosamines,[11] soft NO^+ species,[12] trifluoroacetic anhydride,[13] m-chloroperbenzoic acid,[14] $NOBF_4$,[15] clayfen,[16] p-nitrobenzaldehyde/TMSOTf,[17] 2-nitrobenzenesulfonyl chloride/potassium superoxide,[18] clayfen or

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clayan/MW,[19] Caro's acid supported on silica gel,[20] manganese dioxide,[21] ceric ammonium nitrate,[22] oxone,[23] $(n\text{-}BuPPh_3)_2S_2O_8$,[24] $(n\text{-}BuPPh_3)_2Cr_2O_7$,[25] 3-carboxypyridinium, and 2,2′-bipyridinium chlorochromates[26] have been reported for oxidation of thiocarbonyl compounds to their oxygen analogues. Unfortunately, most of these reagents suffer from at least one of the following disadvantages: (i) long reaction time, (ii) no selectivity, (iii) tedious work-up procedure, (iv) cost of preparation, and (v) low yields of the products.

Recently, much attention has been focused on the use of quaternary ammonium salts [such as tetrabutylammonium periodate ($n\text{-}Bu_4N^+IO_4^-$)] for a variety of functional group transformations in homogeneous phase in non-aqueous solvents.[27] The solubility of quaternary ammonium periodate in several solvents provides advantages, such as low reaction temperatures, high reaction rates, absence of side reactions, and higher yields. However, some of them need catalysts for activation.

The use of solid supports in synthetic organic chemistry has become more important in recent years due to their characteristic properties such as the enhanced selectivity and reactivity and the convenient product isolation they provide.[28]

Both the Bronsted and Lewis acidic sites of the acidic solid supports are involved in the generation of active species of periodate,[29] which may be either IO_4^- or H_5IO_6 depending on the site acidity.

RESULT AND DISCUSSION

A variety of thioamides (primary, secondary, and tertiary) were treated with $n\text{-}Bu_4N^+IO_4^-$/acidified, wet SiO_2 under solid phase conditions at room temperature; they afforded the corresponding amides in good to excellent yields (Entries 1–15, Table I).

As shown in Table II, in the absence of acid, the conversion yields of thioamide decreased to 5–10%, and without SiO_2, no reaction is observed. The maximum yields were observed when concentrated HCl was applied for the preparation of catalyst.

For the investigation of the deprotection of larger amounts of the thioamides, 10 mmol of some thioamides was applied in the reaction. The results were comparable to those of small scale experiments; therefore, this method is also applicable for operation on a molar scale. It was found that in these reactions, sulfur is converted to sulfate and replaced by oxygen, which is indicated by the addition of a solution of $BaCl_2$.

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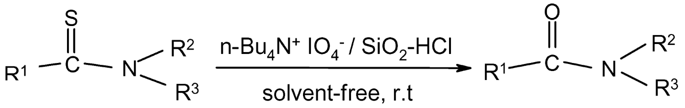
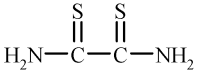
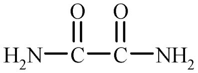
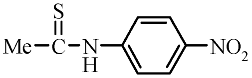
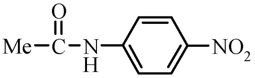
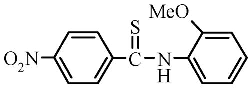
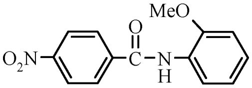
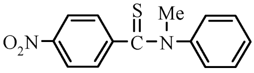
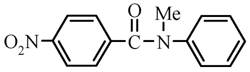
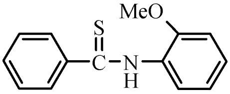
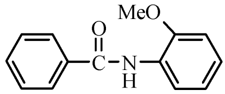
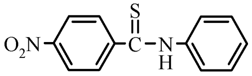
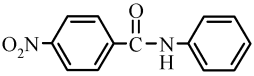
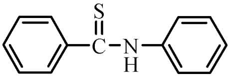
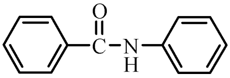
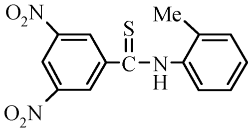
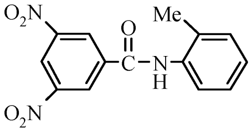
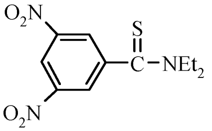
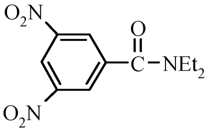
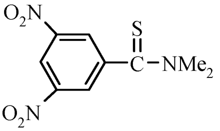
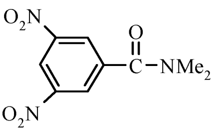
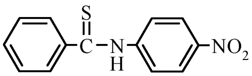
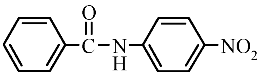
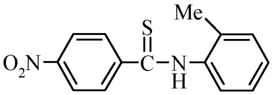
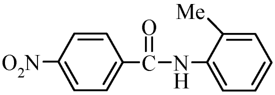
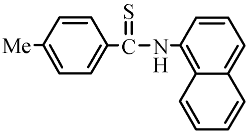
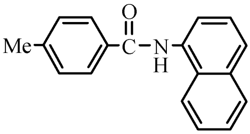
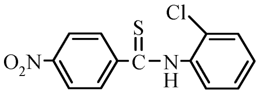
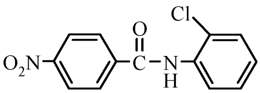
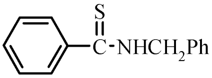
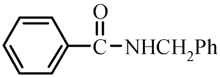
TABLE I Transformation of Thioamide Derivatives to the Corresponding Amides with n-Bu$_4$N$^+$IO$_4^-$/Acidified, Wet SiO$_2$



Entry	Thioamides	Amides	Time (min)	Yields (%)
1			5	93
2			2	97
3			4	94
4			5	91
5			11	96
6			2	95
7			7	96
8			2	96
9			4	92
10			2	94
11			5	97

(Continued on next page)

TABLE I Transformation of Thioamide Derivatives to the Corresponding Amides with n-$Bu_4N^+IO_4^-$/Acidified, Wet SiO_2 *(Continued)*

Entry	Thioamides	Amides	Time (min)	Yields (%)
12			3	91
13			3	91
14			2	93
15			8	92

In conclusion, we have developed a mild and convenient procedure for the conversion of thioamides to amides using n-$Bu_4N^+IO_4^-$/acidified, wet SiO_2 as a nontoxic and inexpensive reagent under solvent-free conditions.

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.[30]

TABLE II Solvent-Free Deprotection of N-Thiobenzoylaniline (7) with n-$Bu_4N^+IO_4^-$ Under Different Conditions

	Condition[a]	Time (min)	Isolated yields (%)
1	Absence of SiO_2	—	No reaction
2	Dry SiO_2	7	5
3	Wet SiO_2	7	10
4	Acidified SiO_2 with 2M HCl solution	7	20
5	Acidified SiO_2 with concentrated HCl	7	>95

[a]The optimized molar ratio of the oxidant/substrate is 1:1.

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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 n-$Bu_4N^+IO_4^-$ (1 mmol, 0.433 g) with acidified, wet silica gel (3.0 g) using a pestle and mortar until a fine, homogeneous, purple powder was obtained. A mixture of thioamide (1 mmol) and n-$Bu_4N^+IO_4^-$/acidified, wet SiO_2 (1 mmol, 3.433 g) was ground with a pestle in a mortar until the TLC showed complete disappearance of the thioamide, which required 2–11 min (Table I). Ethylacetate (2 × 10 mL) was added to the reaction mixture, and after vigorous stirring was filtered through a sintered glass funnel and the solvent was then evaporated under vacuum. The solvent was evaporated, and the crude product was purified by column chromatography on silica gel using ethyl acetate as an eluent. The pure products were obtained in 91–97% yields.

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