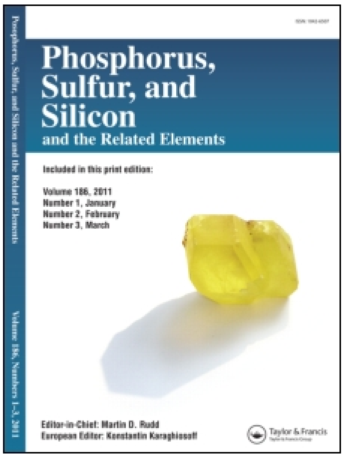

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TRANSFORMATION OF THIOAMIDE COMPOUNDS TO CORRESPONDING AMIDES USING 12-TUNGSTOSILICIC ACID

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12-Tungstosilicic acid ($H_4SiW_{12}O_{40}$) is applied for the conversion of a series of thioamides to their corresponding oxo analogues in excellent yields in acetonitrile. In the case of thioketones, no reaction is observed under these conditions. The reusability of the catalyst also is investigated.

Keywords Amide; oxidations; thioamides; transformation; 12-tungstosilicic acid

INTRODUCTION

In recent years, catalysis of Keggin-type heteropoly acids (HPAs), typically represented by the formula $H_{8-x}[XM_{12}O_{40}]$, where X is the heteroatom (e.g., P^{5+} or Si^{4+}), x is its oxidation state, and M is the addenda atom (usually W^{6+} or Mo^{6+}), has attracted much interest, especially tungstophosphoric acid ($H_3PW_{12}O_{40}$), tungstosilicic acid ($H_4SiW_{12}O_{40}$), and molybdatophosphoric acid ($H_3PMo_{12}O_{40}$).[1] These are promising materials that have strong acidity as well as oxidizing ability with greater activity than the conventional catalysts, such as mineral acids, zeolites, ion-exchange resins, and H_3PO_4/SiO_2[2,3] and are used as a catalyst for various kinds of organic transformations.[4–7]

Heteropoly acids have several advantages as catalysts because of their flexibility in modifying the acid strength, their environmental compatibility, nontoxicity, and experimental simplicity, which make them economically and environmentally attractive.[2a,8,9] Heteropolyacids have been extensively studied because of their interesting catalytic properties for the synthesis of antioxidants, medicinal preparations, vitamins, and biologically active substances.[10,11]

HPAs have several advantages over liquid acid catalysts, including being noncorrosive and environmentally benign. In aqueous solution, these compounds such as PW, SiW, and PMo are strong, fully dissociated acids. HPAs in solution are stronger than the usual

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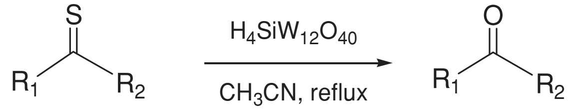
mineral acids such as H_2SO_4, HNO_3, HCl, and HBr, and even strong acids such as $HClO_4$ and CF_3SO_3H.[2a] Among heteropolyacids, polytungstic acids are the most widely used catalysts owing to their high acidic strength, thermal stability, and low reducibilities.

From a synthetic point of view, the transformation of thioamides to their corresponding amides is an important reaction in 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.[12] For this conversion, various methods and reagents such as *t*-butyl hypochlorite,[13] dimethyl selenoxide,[14] benzeneseleninic anhydride,[15] thiophosgene,[16] dimethyl sulfoxide/iodine,[17] $NOBF_4$,[18] soft NO^+ species,[19] trifluoroacetic anhydride,[20] *p*-nitrobenzaldehyde/TMSOTf,[21] manganese dioxide,[22] clayfen or clayan/MW,[23] Caro's acid supported on silica gel,[24] oxone,[25] $(n\text{-BuPPh}_3)_2S_2O_8$,[26] $(n\text{-BuPPh}_3)_2Cr_2O_7$,[27] 3-carboxypyridinium and 2,2'-bipyridinium chlorochromates,[28] and tetrabutylammonium periodate[29] have been reported. However, some of these methods are not suitable for conversion of primary thioamides, and some also show limitations such as low yields of the products, long reaction times, the use of expensive reagents, and tedious workup procedures.

RESULTS AND DISCUSSION

In continuation of our ongoing research program,[30] we wish report a mild and efficient transformation of thioamides into the corresponding amides using tungstosilicic acid. Various thioamides were reacted with the $H_4SiW_{12}O_{40}$ in acetonitrile at reflux to afford the corresponding amides in excellent yields (Scheme 1).



R_1: alkyl, aryl
R_2: alkyl, aryl (thioketones)
or NRR' (thioamides, R,R': H, alkyl, aryl)

Scheme 1 Transformation of thioamides to their corresponding amides.

In choosing the reaction media, different solvents were investigated in the conversion of N-thiobenzoylaniline to N-benzoylaniline with $H_4SiW_{12}O_{40}$ under reflux conditions. Among the studied solvents, CH_3CN was chosen as suitable solvent because higher amide derivatives were observed (Table I). By employing 0.5 molar equivalent of the reagent in CH_3CN, the amide was obtained after 90 min in 96% yield. These conditions were applied for the conversion of different thioamides into their corresponding amides.

As shown in Table II, a variety of primary, secondary, and tertiary thioamides were treated with tungstosilicic acid in refluxing acetonitrile to afford the corresponding carbonyl compounds in excellent yields (Table II, entries 1–15). In the case of thioketones such as thiobenzophenone or 3-thiopentanone, no reaction was observed under these conditions. Therefore thioamides can be selectively converted to amide analogues in the presence of thioketones.

Large scale deprotection of some thioamides to their corresponding amides was also investigated. The results were comparable to those of small scale experiments; therefore, it

Table I Conversion of N-thiobenzoyl aniline to corresponding amide with $H_4SiW_{12}O_{40}$ in different solvents under reflux conditions

Solvent	$H_4SiW_{12}O_{40}$(mmol)	Time (min)	Yield (%)[a]
H_2O	0.5	90	40
CH_2Cl_2	0.5	90	10
CCl_4	0.5	90	10
CH_3CH_2OH	0.5	90	7
CH_3OH	0.5	90	8
$CHCl_3$	0.5	90	5
CH_3COCH_3	0.5	90	0
CH_3CN	1	90	90
CH_3CN	0.5	90	97
CH_3CN	0.25	150	25

[a] Isolated yields.

seems that this method is also applicable for operation on a large scale desulfurization of thioamides.

The reusability of the catalyst was monitored using multiple sequential conversion of N-thiobenzoyl aniline as a typical thioamide with tungstosilicic acid. For each of the repeated reactions, the catalyst was recovered and dried before being used for fresh thioamide. The catalyst was consecutively reused four times without a detectable catalyst leaching or a significant loss of its activity (Table III).

In order to detail the ability of our method with respect to previous reports, some of our results in comparison with some other methods are summarized in Table IV. As is shown, the yield/time ratios of our present method are better or comparable with others.

Table II Transformation of thioamide derivatives to their corresponding amides with $H_4SiW_{12}O_{40}$ in acetonitrile[a]

					Mp (°C)	
Entry	R_1	R_2	Time (min)	Yields[b](%)	Found	Reported[34]
1	H_2NCS	NH_2	90	97	298–299	>300[34b]
2	C_6H_5	C_6H_5NH	90	96	160–162	163[34a]
3	$4\text{-}NO_2C_6H_4$	$2\text{-}CH_3C_6H_4NH$	100	95	152–154	155[34c]
4	$4\text{-}NO_2C_6H_4$	$2\text{-}CH_3OC_6H_4NH$	110	94	146–147	148[34c]
5	$4\text{-}NO_2C_6H_4$	$C_6H_5NCH_3$	150	90	105–107	107[34c]
6	C_6H_5	$C_6H_5CH_2NH$	120	93	150–152	152–153[34b]
7	CH_3	$4\text{-}NO_2C_6H_4NH$	120	94	215–217	215–216[34b]
8	$3,5\text{-}(NO_2)_2C_6H_3$	$2\text{-}CH_3C_6H_4NH$	90	97	239–240	241–242[34c]
9	$4\text{-}NO_2C_6H_4$	$2\text{-}ClC_6H_4NH$	90	95	159–160	160[34c]
10	$4\text{-}NO_2C_6H_4$	C_6H_5NH	120	93	210–212	211[34b]
11	$3,5\text{-}(NO_2)_2C_6H_3$	$(CH_2CH_3)_2N$	90	90	87–88	89–91[34c]
12	$4\text{-}CH_3C_6H_4$	1-naphthyl-NH	90	95	169–170	173[34c]
13	C_6H_5	$2\text{-}CH_3OC_6H_4NH$	100	94	59–61	60[34a]
14	C_6H_5	$4\text{-}NO_2C_6H_4NH$	120	93	200–202	199–200[34b]
15	$3,5\text{-}(NO_2)_2C_6H_3$	$(CH_3)_2NH$	100	90	127–129	128–130[34c]

[a] All products were identified by comparison with authentic samples (IR, ^1H NMR, mp).
[b] Isolated yields.

Table III Reusability of $H_4SiW_{12}O_{40}$ in conversion of N-thiobenzoyl aniline

Row	Time (min)	Yields (%)
1	90	96
2	90	95
3	95	95
4	100	93

In conclusion, we have developed an efficient procedure for the conversion of thioamides to their carbonyl compounds using tungstosilicic acid in acetonitrile, as a simple and inexpensive reagent under reflux conditions. The appropriate reaction times, high product yields, easy workup, and reusability of the catalyst 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[31,32] and thioketones[33] were prepared according to described procedures.

General Procedure for the Conversion of Thiocarbonyls to Carbonyl Compounds in Acetonitrile Solvent

In a round bottomed flask (25 mL), a solution of thiocarbonyl compound (1 mmol) in CH_3CN (10 mL) was treated with $H_4SiW_{12}O_{40}$ (0.5 mmol), and the reaction mixture was stirred under reflux for the time indicated in Table II. The progress of the reaction was monitored by TLC (eluent: CCl_4:EtOAc, 10:1). After completion, diethyl ether (2 × 10 mL) was added to the reaction mixture and the crude product was extracted. The solvent was evaporated, and the crude product was purified by column chromatography on silica-gel and recrystallized from *n*-hexane to afford the pure product.

Table IV Comparison of some of our results with those reported in the literature[a]

Entry[b]	A[c]	B	C	D	E
1	97/90	85/180	84/40	85/10	93/30
2	96/90	—	81/80	90/15	95/30
3	95/100	—	—	78/25	93/55
5	90/150	90/180	—	90/25	94/10
7	94/120	—	—	95/20	—
10	93/120	—	—	90/30	92/70
12	95/90	—	90/30	—	95/20

[a] Values refer to yield (%)/time (min) ratios.

[b] The entries refer to those in Table II.

[c] A: Our method; B: Ag_2CO_3/Celite, CH_3CN, r.t.;[35] C: n-$Bu_4N^+IO_4^-/CH_2Cl_2$, r.t.;[29] D: Oxone/Solid phase;[25b] E: (n-$BuPPh_3)Cr_2O_7/CH_3CN$, reflux.[27]

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