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Facile Desulfurization of Thioamides and Thioureas with Tetrabutylammonium Periodate under Mild Conditions

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Summary. Thioamides and thioureas were reacted with tetrabutylammonium periodate at room temperature to afford the corresponding amides and ureas, respectively, under aprotic conditions.

Keywords. Oxidation; Thiocarbonyl; Quaternary ammonium salt; Periodate.

Introduction

Thiocarbonyl compounds are specific and versatile tools for multi-step synthetic routes leading to various natural products or biologically active molecules [1]. However, final step of a total synthesis may involve transformation of a thiocarbonyl group into the corresponding carbonyl group. Several methods have been developed for conversion of the thiocarbonyl groups into oxo analogues [2].

In recent years, desulfurization of thioamides and thioureas has found great interest in synthetic organic chemistry. For this transformation, many reagents have been reported in the literature such as dinitrogen tetroxide [3], $NOBF_4$ [4], *N*-nitrosamines/KI/HCl [5], *t*-butyl thionitrate [6], *t*-butyl hypochlorite [7], $NaNO_2$/HCl [8], superoxide [9], Br_2/OH^- [10], metal nitrates [11], ceric ammonium nitrate [12], thiophosgene [13], thionyl chloride [14], gold(III) halogenides [15], SeO_2 [16], potassium bromate in alkaline solution [17], OsO_4 [18], *m*-chloroperbenzoic acid [19], alkaline peroxide [20], H_2O_2 [21], $KMnO_4$ [22], MnO_2 [23], dimethyldioxirane [24], dimethylsulfoxide/I_2 [25], *N*-bromosuccinimide [26], trifluoroacetic anhydride [27], *Caro*'s acid supported on silica gel [28], oxone [29], $(n\text{-}BuPPh_3)_2S_2O_8$ [30a], $(n\text{-}BuPPh_3)_2Cr_2O_7$ [30b], and 3-carboxypyridinium and 2,2′-bipyridinium chlorochromates [30c]. However, many of these methods suffer from limitations such as long reaction times, using expensive, toxic, or commercially non-available reagents, and tedious work-up. Furthermore some of them are

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not suitable for desulfurization of primary thioamides and thioureas. Consequently, there is continued interest in developing new and convenient methods for this conversion under mild reaction conditions.

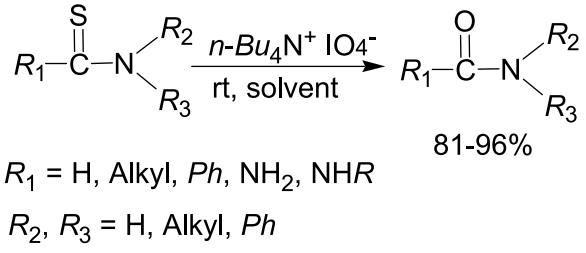
However the use of quaternary ammonium salts for this reaction has not been considered yet. Tetrabutylammonium periodate (n-Bu_4N^+ IO_4^-) has been extensively used as an efficient oxidant for a variety of functional group transformations in organic synthesis [31]. The solubility of this salt in several solvents, low reaction temperatures, and absence of side reactions provide advantages of the reagent when used in organic synthesis.

Results and Discussions

In continuation of our ongoing research program on the use of quaternary ammonium salts as reagents [32], we now report mild and efficient conversion of thioamides and thioureas into the corresponding oxo compounds by using tetrabutylammonium periodate. As shown in Scheme 1, various thioamides and thioureas were reacted with the reagent at room temperature to afford the corresponding amides or ureas in good to excellent yields.

In order to optimize the reaction conditions at first the effect of solvent for conversion of thiobenzamide to benzamide with n-Bu_4N^+ IO_4^- was examined at room temperature (Table 1).

We found that using CH_2Cl_2 as solvent gave the best result for this conversion. By employing 0.5 molar equivalents of the reagent in CH_2Cl_2, benzamide was obtained after 5 minutes in 93% isolated yield. These conditions were applied



Scheme 1

Table 1. Conversion of thiobenzamide to benzamide with n-Bu_4N^+ IO_4^- in different solvents at room temperature

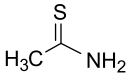
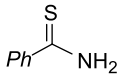
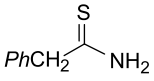
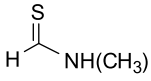
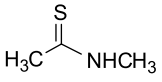
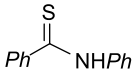
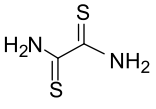
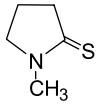
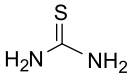
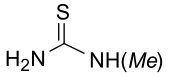
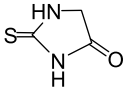
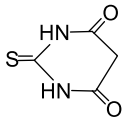
Entry	Solvent	n-Bu_4N^+ IO_4^-/mmol	Time/min	Yield/%[a]
1	Acetone	0.5	300	35
2	*EtOAc*	0.5	180	80
3	CH_3CN	0.5	80	90
4	Benzene	0.5	10	88
5	CH_2Cl_2	1	2	92
6	CH_2Cl_2	0.5	5	93
7	CH_2Cl_2	0.25	90	60

[a] Yield of isolated product

for conversion of structurally different thioamides into their corresponding amides. For thioureas best results were obtained when a mixture of CH_3CN and CH_2Cl_2 (1:1) was used as reaction medium. In the case of thioketones such as thiobenzophenone no reaction was observed under these conditions.

As shown in Table 2, various thioamides and thioureas efficiently were converted to the corresponding oxo compounds by this method. Primary and

Table 2. Desulfurization of thioamides and thioureas with *n-Bu*$_4$N$^+$ IO_4^- at room temperature

Entry	Substrate	Solvent	Time/min	Yield/%[a]
1[b]		CH_2Cl_2	2	96
2[b]		CH_2Cl_2	5	93
3[b]		CH_2Cl_2	7	89
4[b]		CH_2Cl_2	45	86
5[b]		CH_2Cl_2	65	82
6[b]		CH_2Cl_2	80	81
7[c]		CH_2Cl_2	40	84
8[c]		CH_2Cl_2	120	81
9[b]		CH_2Cl_2:CH_3CN (1:1)	25	90
10[b]		CH_2Cl_2:CH_3CN (1:1)	35	88
11[c]		CH_2Cl_2:CH_3CN (1:1)	120	84
12[c]		CH_2Cl_2:CH_3CN (1:1)	120	86

[a] Yield of isolated product; all amides and ureas have been described in literature and were identified by their IR spectra and melting points; [b] 0.5 mmol of the reagent were used; [c] one mmol of the reagent was used

secondary thioamides and thioureas were reacted with *n*-Bu_4N^+ IO_4^- at room temperature to afford the corresponding amides or ureas at mild and aprotic reaction conditions in good yields.

In conclusion, our procedure provides a selective and efficient method for desulfurization of thioamides and thioureas under aprotic conditions using tetrabutylammonium periodate as a cheap and commercially available reagent. Mild reaction conditions, simple setup and workup, and solubility of the reagent in most organic solvents are other advantages of the method.

Experimental

Chemicals were obtained from Merck and Fluka chemical companies. FT-IR spectra were recorded on a Perkin Elmer RXI spectrometer. NMR spectra were recorded on a Brucker Avance DPX 250 MHz instrument. The products were purified by column chromatography and the purity determination of the products was accomplished by GLC on a Shimadzu model GC 10-A instrument or by thin layer chromatography on silica gel polygram on SIL G/UV 254 plates.

Typical Procedure for the Conversion of Thiobenzamide to Benzamide

To a solution of thiobenzamide (0.274 g, 2 mmol) in 10 cm^3 of methylene chloride was added *n*-Bu_4N^+ IO_4^- (0.433 g, 1 mmol) at room temperature and the resulting mixture was stirred for 5 min. The mixture becomes purple upon completion of the reaction. Then the mixture was washed with 10% sodium thiosulfate solution (2×10 cm^3) and distilled water (2×10 cm^3). The organic phase was dried with sodium sulfate and then filtered through a short column containing silica gel. Removal of the solvent under reduced pressure afforded benzamide; yield 0.225 g (93%); mp 133–135°C (Ref. [33] 132–133°C).

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