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$TiCl_4$-promoted desulfurization of thiocarbonyls and oxidation of sulfides in the presence of H_2O_2

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$TiCl_4$-promoted desulfurization of thiocarbonyls and oxidation of sulfides in the presence of H_2O_2

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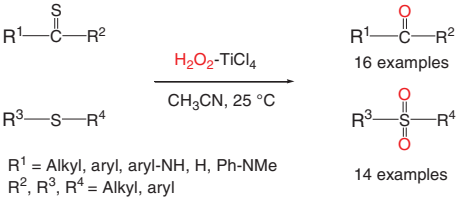
H_2O_2 in combination with $TiCl_4$ proved to be a highly reactive reagent system for the desulfurization of thioamide and thioketone derivatives in excellent yields and short reaction times with high purity. Sulfides were also found to undergo oxidation to sulfones under similar reaction conditions. In most cases, these reactions are highly selective, simple, and clean, affording products in high yields and purity.



Keywords: desulfurization; thioamides; thioketones; sulfones; titanium tetrachloride

1. Introduction

Functional group manipulations are of paramount importance to synthetic organic chemists and hence the development of novel transformations still remains of great interest (*1*). The conversion of thiocarbonyl compounds to their carbonyl compounds has received considerable attention. Among carbonyl compounds, amides are important commercial and biological compounds. Because amides constitute the backbone of protein molecules, their chemistry is of extreme importance. The penicillin and cephalosporin antibiotics (Figure 1) are among the best known products of the pharmaceutical industry (*2*). In recognition of their importance, several reagents such as sodium peroxide (*3*), *t*-butyl hypochlorite (*4*), diaryl telluroxide (*5*), singlet

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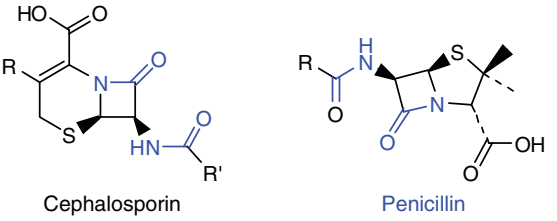


Figure 1. Structures of organic amides used as drug candidates.

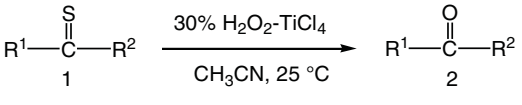
oxygen (*6*), benzeneseleninic anhydride (*7*), thiophosgene (*8*), dimethyl sulfoxide/iodine (*9*), *m*-chloroperbenzoic acid (*10*), soft NO^+ species (*11*), trifluoroacetic anhydride (*12*), clay-supported ferric nitrate (*13*), manganese dioxide (*14*), and bismuth(III) nitrate (*15*) are available for the oxidation of thioamides to their oxygen analogs.

However, the reported methods rarely offer the ideal combination of simplicity of procedure, fast and selective reactions, and high yields of products and often suffer from a lack of generality and economic applicability. As a consequence, the introduction of new methods and/or further work on technical improvements to overcome the limitations is still an important experimental challenge.

Titanium tetrachloride is a valuable reagent promoting various synthetic reactions, both in the cases requiring a stoichiometric amount of $TiC1_4$ and in those requiring a catalytic amount of $TiCl_4$ together with other metal salts (*16*).

Aqueous hydrogen peroxide (30%) is an ideal oxidant in view of its high effective oxygen content, its eco-friendly byproduct (water), its relative safety in storage and operation, and its comparatively low cost of production and transportation (*17*). These advantages inspired us to explore the potential of H_2O_2 in combination with $TiC1_4$ for the desulfurization of thioamides.

As part of an ongoing program directed at the development of efficient reagents for use under mild conditions and following our latest interest in the use of hydrogen peroxide in organic synthesis (*18*), we envisaged that a combination of H_2O_2 with $TiC1_4$ could bring about the selective desulfurization of thioamides. To our knowledge, there are no literature reports on the conversion of thioamides to the corresponding amides by the use of H_2O_2–$TiC1_4$ system (Scheme 1).



Scheme 1. Desulfurization of thiocarbonyls.

2. Results and discussion

To evaluate the solvent effect, the reaction of *N*-(4-bromophenyl)thioacetamide as the model compound was carried out under similar reaction conditions using various organic solvents. Among the various solvents such as chloroform, dichloromethane, toluene, acetonitrile, and ethanol used for this transformation, acetonitrile was the solvent of choice as the best results were obtained with it.

To arrive at an optimum stoichiometry, when *N*-(4-bromophenyl)thioacetamide (1 mmol) was allowed to react with 0, 1, 2, and 3 equivalent of H_2O_2 in the presence of different amounts of $TiCl_4$ at 25°C, the yields of the product obtained were 5%, 50%, 80%, 96%, and 95%, respectively. As a result, higher amounts of H_2O_2 neither increased the yield nor lowered the reaction time, and $TiCl_4$ was an effective agent only in the presence of H_2O_2. Therefore, the best result in 96%

Table 1. Effect of increasing amounts of H_2O_2 and $TiCl_4$ on the desulfurization of *N*-(4-bromophenyl)thioacetamide.[a]

Entry	$TiCl_4$ (mmol)	30% H_2O_2 (mmol)	Yield%[b]
1	1	0	5
2	0.8	1	50
3	0.8	2	80
4	1	2	96
5	1	3	95

Notes: [a]Reaction conditions: The reactions were performed with *N*-(4-bromophenyl)thioacetamide (1 mmol) for 2 min at 25°C.
[b]Isolated yield.

yield was obtained by carrying out the reaction with 1:2 mol ratios of thioamide to H_2O_2 in the presence of 1 mmol $TiC1_4$ for 2 min (Table 1).

Under these optimized reaction conditions, the generality and scope of this new desulfurization protocol were then explored. A range of structurally diverse thioamides were subjected under optimized reaction conditions to produce the corresponding amide derivatives. The results are given in Table 2. Aromatic thioamides having electron-donating and electron-withdrawing groups in the aromatic ring afforded excellent yields of products irrespective of the electronic effects.

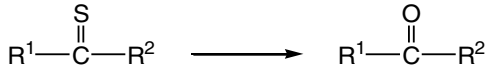
Notably, primary, secondary, and tertiary thioamides underwent this reaction with equal efficiency. For example, benzamide (Table 2, Entry 13) was produced in 95% yield, *N*-phenyl benzamide (Table 2, Entry 1) in 96% yield, and *N*-methyl-4-nitro-*N*-phenylbenzamide (Table 2, Entry 9) in 93% yield. Furthermore, it worked well with a variety of thioketones, and a representative list of the compounds used to test the above reaction is given in Table 2 along with the excellent yields and the melting points of the corresponding oxo compounds thus obtained. Steric effects did not influence the yield significantly; for example, thiocamphor (Table 2, Entry 14) and fluorene-9-thione (Table 2, Entry 16) gave the desired ketones in 92% and 93% yields, respectively. The functional group tolerance of this method is evident from Entry 15 because the sulfur group was unaffected under the reaction conditions.

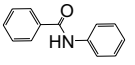
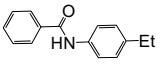
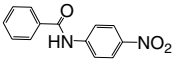
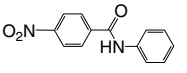
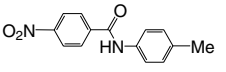
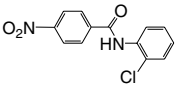
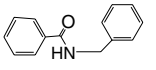
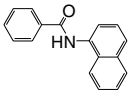
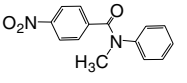
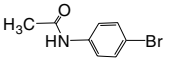
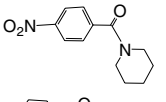
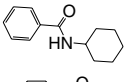
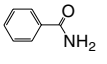
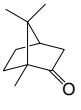
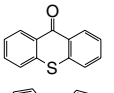
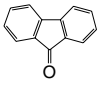
Since the oxidation of thioamides and thioketones proved the potential of $TiC1_4$ as an effective and mild promoter agent, the oxidation of sulfides to the corresponding sulfones was studied. Sulfones are useful synthetic intermediates for the construction of various chemically and biologically significant molecules (*19*). Despite a number of alternative methods available for the synthesis of sulfones, the oxidation of sulfides to sulfones is much less investigated compared with the oxidation of sulfides to sulfoxides. However, the oxidation of sulfides to sulfones is the most favored method. The popularity of this method is due to the availability of a wide variety of sulfides that can be utilized in the oxidation of sulfides to the corresponding sulfones.

A survey of the literature revealed that several methods have been reported for the oxidation of sulfides to sulfones (*20–22*). Many of these are not practical in some respects, such as prolonged reaction times, low yields, undesired side reactions occurring on other functional groups, not readily available reagents, and harsh reaction conditions. Therefore, a need for the development of an easy and efficient reagent for the conversion of sulfides to sulfones still exists. In this paper, we describe the successful use of the H_2O_2–$TiC1_4$ system as an efficient method for this purpose (Scheme 2).

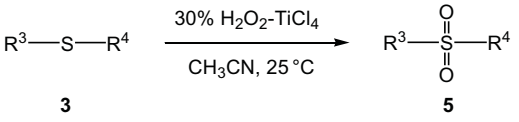
The optimum molar ratio of sulfide to H_2O_2 to $TiC1_4$ (1:4:1) was found to be ideal for the complete conversion of sulfide into sulfone in acetonitrile at room temperature, while with lesser amounts (*e.g.* 1:4:0.75 and 1:3:1), the reaction remained incomplete and increased sulfoxide contamination, thereby reducing the selectivity of the oxidation.

Table 2. Selective desulfurization of thiocarbonyls.[a]



Entry	product	Yield/%[b] (*t*/min)	Mp/°C (Lit. Mp.)	References
1		96 (2)	162–163 (158–162)	(*18p*)
2		91 (2)	148 (149)	(*18e*)
3		93 (2)	196–198 (195–197)	(*18e*)
4		90 (2)	209–210 (208)	(*18e*)
5		95 (2)	200–201 (200–202)	(*18e*)
6		95 (2)	160 (157–158)	(*18e*)
7		93 (2)	103–105 (105–106)	(*23*)
8		90 (2)	164 (164–165)	(*24*)
9		93 (2)	105–107 (104)	(*18p*)
10		96 (2)	165–167 (168)	(*18p*)
11		92 (2)	121–123 (121)	(*18e*)
12		94 (2)	144–145 (147)	(*25*)
13		95 (2)	129 (129)	(*26*)
14		92 (2)	180–181 (180–182)	(*26*)
15		93 (2)	210 (209)	(*18e*)
16		93 (2)	83–84 (80)	(*18p*)

Notes: [a]The products were characterized by comparison of their spectroscopic and physical data with those of authentic samples synthesized by the reported procedures.
[b]Yields refer to pure isolated products.



Scheme 2. Oxidation of sulfides to sulfones.

The choice of the organic solvent is of particular importance. Acetonitrile and 1,4-dioxane were found to be suitable, giving rise to a relatively fast reaction rate at room temperature. If the reactions are carried out in other less polar solvents such as dichloromethane, chloroform, or some ethers, they become quite sluggish and usually do not reach completion.

Under the optimized conditions, the oxidation of several kinds of sulfides was carried out. The results are given in Table 3. The aromatic and aliphatic and cyclic and acyclic sulfides can be oxidized to sulfones in good to excellent yields. Both electron-rich and electron-deficient aryl sulfides worked pretty well, mostly leading to excellent yields of products. In terms of reactivity, aryl sulfides including electron-poor groups react slowly than those with electron-rich groups. For example, the reaction of 4-nitrobenzyl phenyl sulfide remains incomplete even after a long reaction time.

The chemoselectivity is noteworthy. Under such conditions, the sulfide function is highly reactive, and various other functional groups are tolerable. For example, 2-hydroxyethyl phenyl sulfide (Table 3, Entry 9) was oxidized to the sulfone products without dehydrogenation of the alcohol function. Oxidation of 2-(phenylthio)acetic acid (Table 3, Entry 10) proceeded smoothly to produce the corresponding sulfone without interference from the carboxyl functional group.

Acid-sensitive sulfides such as 2-[(benzylthio)methyl] furan (Table 3, Entry 8) and methyl 2-(phenylthio)acetate (Table 3, Entry 11) worked well without the formation of any side products, which are normally observed in the presence of either protic or Lewis acids. Allylic sulfide (Table 3, Entry 12) yielded the corresponding sulfone without affecting the C9C bond. Also, the protocol worked efficiently in oxidizing 2-(methylthio)-1H-benzo[d]imidazole (Table 3, Entry 7) to afford the corresponding sulfone.

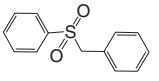
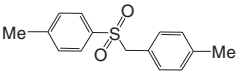
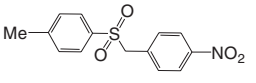
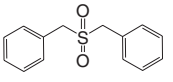
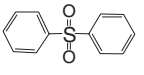
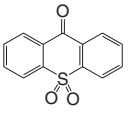
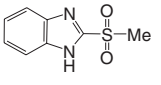
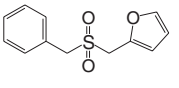
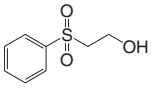
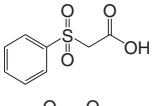
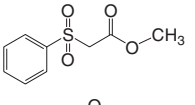
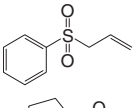
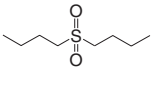
To further determine the scope of the reaction, a mixed reaction was carried out with benzyl phenyl sulfide and 4-methylbenzaldehyde. After 2 min, the complete selective oxidation of sulfide to sulfone occurred and 4-methylbenzaldehyde remained unreacted. Prolonging the reaction time to 2 h did not result in any change.

The possible mechanism of the reaction is outlined in Scheme 3. Initially, an orange-red solution was obtained, which may be due to the formation of complex (**6**) between titanium tetrachloride and hydrogen peroxide (*31*). The oxygen atom in this complex is more electrophilic. Therefore, the mechanism proceeds probably through the nucleophilic attack of sulfur atom in thioamide (**1**) and sulfide (**3**) on this complex as shown in Scheme 3. In the case of sulfone formation, sulfoxide (**4**) further reacts with the intermediate (**7**) to form sulfone (**5**) and leads to the eventual generation of TiO_2.

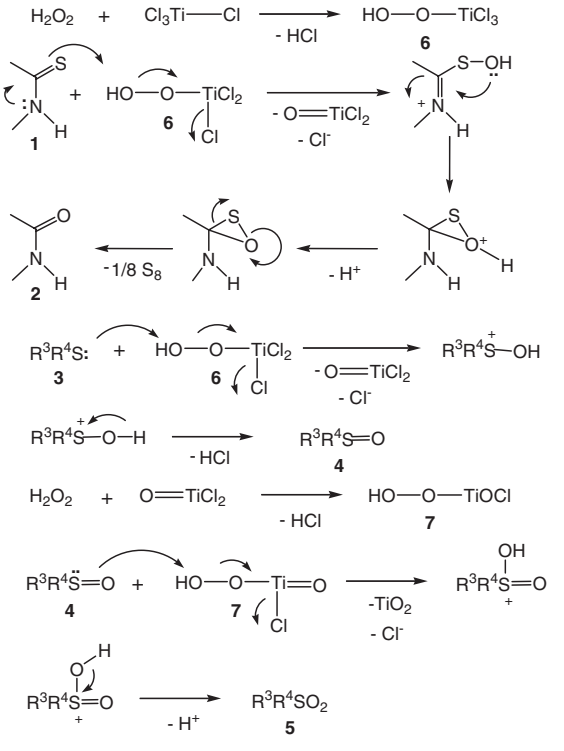
3. Conclusion

In summary, a specific selective oxidative protocol using the H_2O_2–$TiCl_4$ reagent system was found to be very useful for the desulfurization of thioamides and thioketones to their corresponding amides and ketones in excellent yields and short reaction times. This reagent system was also found to be a mild and efficient oxidizing agent for the oxidation of sulfides to the corresponding sulfones in good to excellent yields. The reaction was highly selective, simple, and clean in most cases.

Table 3. Selective oxidation of sulfides into sulfones.[a]

Entry	Sulfone	Yield/%[b] (*t*/min)	Mp/°C (Lit. Mp.)	References
1		95 (2)	147 (146–147)	(*18q*)
2		90 (3)	157 (156–157)	(*27a*)
3[d]		80 (20)	180–182 (180–181)	(*27b*)
4		91 (2)	150 (150–151)	(*27c*)
5		95 (2)	124 (125–126)	(*18q*)
6[c]		95 (2)	187 (186–188)	(*18q*)
7[d]		81 (5)	199–200 (202)	(*28*)
8		90 (10)	84–85 (84–85)	(*18q*)
9[d]		85 (5)	Oil (Oil)	(*29*)
10[d]		83 (5)	110–111 (111)	(*18q*)
11		91 (5)	Oil (Oil)	(*30*)
12		90 (10)	Oil (Oil)	(*18q*)
13		92 (2)	Oil (Oil)	(*27c*)
14		90 (5)	45–46 (46–46.5)	(*29*)

Notes: [a]The purified products were characterized by melting point and ^{1}H and ^{13}C NMR.
[b]Yields refer to pure isolated products.
[c]1,4-Dioxane was used as the solvent.
[d]In these cases, the sulfone products were accompanied by 10–15% of their corresponding sulfoxides.



Scheme 3. Proposed mechanism for the oxidation of thioamides and sulfides.

4. Experimental section

Thiocarbonyls and sulfides either were commercially available or were prepared as follows: thioamides from the reaction of the corresponding amides with P_4S_{10} (*32*), thioketones from the reaction of the corresponding ketones with Lawesson's reagent (*33*), and sulfides from S-alkylation of thiols (*34*). Melting points were determined in a capillary tube and are not corrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker-200 NMR spectrometer using TMS as the internal standard.

4.1. *General procedure for the desulfurization of thioamides and thioketones*

A mixture of thiocarbonyl compound (1 mmol), 30% H_2O_2 (2 mmol, 0.2 ml), and $TiC1_4$ (1 mmol, 0.11 ml) was stirred in CH_3CN at room temperature for 2 min (Table 2). A yellow solid (TiO_2 and elemental sulfur) immediately precipitated. After completion of the reaction as indicated by TLC, the reaction mixture was filtered to give TiO_2 and elemental sulfur. The filtrate was poured into water (10 ml) and extracted with ethyl acetate (4 × 5 ml), and the extract was dried with anhydrous $MgSO_4$. The filtrate was evaporated under vacuum to afford the analytically pure product.

4.2. *General procedure for the preparation of sulfones*

To the mixture of sulfide (1 mmol) and 30% H_2O_2 (4 mmol, 0.4 ml) in acetonitrile (5 ml), $TiC1_4$ (1 mmol, 0.11 ml) was added. The mixture was stirred at room temperature for an appropriate period of time (Table 3). A white solid (TiO_2) immediately precipitated. After the complete

consumption of the starting material as observed by TLC, the reaction mixture was filtered to give TiO_2. The filtrate was poured into water (10 ml). The residue was then extracted with EtOAc (4×5 ml) and the combined extracts were dried ($MgSO_4$). The filtrate was evaporated and the corresponding sulfone was obtained as the only product. In the case of sulfones 3, 7, 9, and 10, the crude product after evaporation of the solvent was purified by column chromatography on silica gel using a mixture of *n*-hexane and ethyl acetate as eluent (90:10).

All the products are known compounds and were characterized easily by comparison with authentic samples (^{1}H and ^{13}C NMR, and melting point).

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