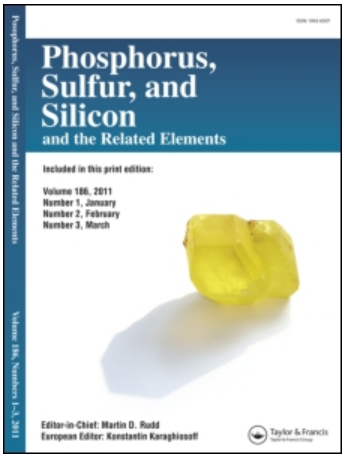

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I. Mohammadpoor-Baltork[a]; M. M. Sadeghi[a]; K. Esmayilpour[a]
[a] Isfahan University, Isfahan, Iran

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A FACILE AND CONVENIENT METHOD FOR DEPROTECTION OF THIOCARBONYLS TO THEIR CARBONYL COMPOUNDS USING OXONE UNDER APROTIC AND NONAQUEOUS CONDITIONS

I. Mohammadpoor-Baltork, M. M. Sadeghi, and K. Esmayilpour
Isfahan University, Isfahan, Iran

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The reaction of oxone as an inexpensive, stable, and commercially available reagent with thiocarbonyl compounds in refluxing acetonitrile has been studied. Primary, secondary, and tertiary thioamides and thioureas are converted to their oxo analogues efficiently. Thiono esters also are transformed to their corresponding esters, while thioketones remained intact under these conditions.

Keywords: Carbonyl compounds; deprotection; oxone; thiocarbonyl compounds

INTRODUCTION

The protection and deprotection of functional groups is of vital importance in synthetic organic chemistry. The conversion of thiocarbonyls to their corresponding carbonyl compounds is a useful transformation in organic synthesis. A wide variety of methods and reagents such as dimethyl selenoxide,[1] diaryl selenoxide,[2] *t*-butyl hypochlorite,[3] diaryl telluroxide,[4] singlet oxygen,[5] bromate or iodate in alkaline solutions,[6] sodium peroxide,[7] benzeneseleninic anhydride,[8] dimethyl sulfoxide/iodine,[9] thiophosgene,[10] $NOBF_4$,[11] *m*-chloroperbenzoic acid,[12] trifluoroacetic anhydride,[13] soft NO^+ species,[14] clay supported ferric nitrate,[15] *p*-nitrobenzaldehyde/TMSOTf,[16] manganese dioxide,[17] 2-nitrobenzenesulfonyl chloride/potassium superoxide,[18] *N*-nitrosamines,[19] clayfen or clayan/MW,[20] and caro's acid supported

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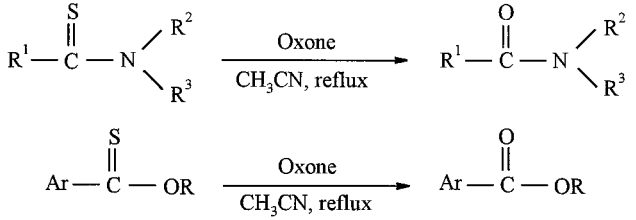
Address correspondence to I. M. Mohammadpoor-Baltork, Department of Chemistry, Isfahan University, Isfahan 81744, Iran. E-mail: imbaltork@sci.ui.ac.ir

on silica gel[21] have been used for the transformation of thiocarbonyl compounds to their corresponding oxo analogues. However, some of these methods are not either suitable for deprotection of primary thioamides or encounter drawbacks such as long reaction times, expensive or toxic reagents, and tedious work-up. Therefore, there is still a need to introduce new methods and inexpensive reagents for such functional group transformations.

RESULTS AND DISCUSSION

Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) is a stable, easily handled, and commercially available oxidizing agent. Recently we introduced oxone as a convenient reagent for the selective deprotection of trimethysilyl and tetrahydropyranyl ethers, ethylene acetals, and ketals.[22] In this article we wish to report an efficient and inexpensive method for the conversion of thiocarbonyls to their corresponding carbonyl compounds with oxone under nonaqueous and aprotic conditions (Scheme 1). Several solvents including acetonitrile, dichloromethane, chloroform, carbon tetrachloride, *n*-hexane, and tetrahydrofuran were investigated during the course of this study. The best results were achieved using acetonitrile.

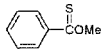
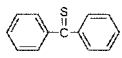
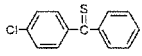
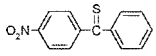
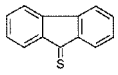


SCHEME 1

The treatment of a series of thioamides and thioureas with oxone in refluxing acetonitrile afforded the corresponding carbonyl compounds in good to excellent yields (Table I, entries 1–31). Thiono esters also were converted to esters in good yields (entries 32, 33). Under the same reaction conditions, thioketones remained unchanged in the reaction mixture (entries 34–37). Therefore, selective deprotection of thioamides and thiono esters in the presence of thioketones is achievable and can be considered as a noteworthy feature of this method.

In summary, we have introduced a convenient and selective method for deprotection of thioamides, thioureas, and thiono esters using

TABLE I Transformation of Thiocarbonyl Compounds to Carbonyl Compounds with Oxone

Run	R^1	R^2	R^3	Oxone (equivalent)	Time (min)	Yield (%)[a]
1	Me	H	H	1	10	90
2	NH_2	H	H	1.5	35	98
3	NH_2	NH_2	H	1.5	30	90
4	NH_2	Ph	H	1.5	15	95
5	PhNH	Ph	H	1.5	25	80
6	$H_2NC{=}S$[b]	H	H	2	60	97
7	$PhN{=}N$	PhNH	H	1.5	30	95
8	Ph	Ph	H	1	16	90
9	Ph	$PhCH_2$	H	1.5	15	97
10	Ph	2-$MeOC_6H_4$	H	1	15	98
11	Ph	2-MeC_6H_4	H	1	15	93
12	Ph	4-$MeOC_6H_4$	H	1	30	95
13	Ph	4-MeC_6H_4	H	1	35	94
14	Ph	4-BrC_6H_4	H	1	35	78
15	Ph	4-$NO_2C_6H_4$	H	1	25	81
16	4-MeC_6H_4	Ph	H	1	25	90
17	4-$NO_2C_6H_4$	Ph	H	1	35	94
18	4-$NO_2C_6H_4$	2-$MeOC_6H_4$	H	1	30	92
19	4-$NO_2C_6H_4$	2-MeC_6H_4	H	1	35	80
20	4-$NO_2C_6H_4$	2-ClC_6H_4	H	1.5	30	77
21	2-ClC_6H_4	4-MeC_6H_4	H	1.5	25	87
22	4-MeC_6H_4	1-Naphthyl	H	1.5	55	80
23	Me	4-BrC_6H_4	H	1	35	95
24	Me	4-$NO_2C_6H_4$	H	1	57	93
25	3,5-$(NO_2)_2C_6H_3$	Ph	H	1	27	75
26	3,5-$(NO_2)_2C_6H_3$	2-MeC_6H_4	H	1	45	70
27	Me	Ph	Me	1.5	40	96
28	4-$NO_2C_6H_4$	Ph	Me	1.5	40	95
29	3,5-$(NO_2)_2C_6H_3$	Me	Me	2	45	87
30	3,5-$(NO_2)_2C_6H_3$	Et	Et	2	40	82
31				2	75	90
32				3	50	85
33				3	55	87
34				3	60	0
35				3	60	0
36				3	60	0
37				3	60	0

[a]Isolated yields.
[b]Oxamide was obtained from the reaction mixture.

oxone, an inexpensive, commercially available and nontoxic reagent. Moreover, the selectivity of the procedure may find application in organic synthesis.

EXPERIMENTAL

General

Thiocarbonyl compounds are either commercially available or were prepared according to described procedures.[23–26] Yields refer to isolated products. All of the products were characterized by comparison of their spectral and physical data with those of authentic samples.

Conversion of Thiocarbonyl Compounds to Their Corresponding Carbonyl Compounds—General Procedure

In a round-bottomed flask (50 ml), a solution of thiocarbonyl compound (1 mmol) in CH_3CN (10 ml) was treated with oxone (1–3 mmol) and the reaction mixture was refluxed for 10–75 min. The progress of the reaction was monitored by TLC (eluent: CCl_4/EtOAc, 4:1). The reaction mixture was filtered and the solid material was washed with CH_3CN (15 ml). The filtrate was evaporated and the crude product was either recrystallized from EtOH/H_2O or subjected to silica gel chromatography using CCl_4/EtOAc, 4:1 as the eluent (Table I).

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