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Bismuth(III) nitrate pentahydrate: a convenient and selective reagent for conversion of thiocarbonyls to their carbonyl compounds

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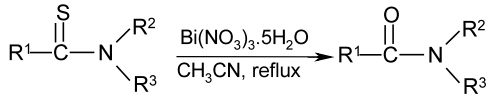
Abstract—A variety of thioamides and thioureas are rapidly transformed to their oxo derivatives with $Bi(NO_3)_3{\cdot}5H_2O$ in excellent yields. However, thiono esters and thioketones are converted to their corresponding carbonyl compounds in only poor yields. $Bi(NO_3)_3{\cdot}5H_2O$ is relatively non-toxic, insensitive to air and inexpensive. These features coupled with the selective deprotection of thioamides and thioureas in the presence of thiono esters and thioketones make this method an attractive alternative to the existing routes for deprotection of thiocarbonyl compounds.

Functional group manipulations are of paramount importance to synthetic organic chemists and hence, the development of novel transformations still remains of great interest. The conversion of thiocarbonyl compounds to their oxygen analogues has received considerable attention. Different methods and reagents such as sodium peroxide,[1] dimethyl selenoxide,[2] diaryl selenoxide,[3] *t*-butyl hypochlorite,[4] bromate or iodate solutions,[5] diaryl telluroxide,[6] singlet oxygen,[7] tetrabutylammonium hydrogensulfate/NaOH,[8] benzeneseleninic anhydride,[9] thiophosgene,[10] dimethyl sulfoxide/iodine,[11] $NOBF_4$,[12] *m*-chloroperbenzoic acid,[13] soft NO^+ species,[14] trifluoroacetic anhydride,[15] clay supported ferric nitrate,[16] manganese dioxide,[17] *p*-nitrobenzaldehyde/TMSOTf,[18] *N*-nitrosoamines,[19] 2-nitrobenzenesulfonyl chloride/potassium superoxide,[20] clayfen or clayan/MW[21] and Caro's acid supported on silica gel[22] have already been reported in the literature for this purpose. However, some of these methods suffer from disadvantages such as long reaction times, the use of toxic or expensive reagents, and difficult workup procedures. Therefore, the introduction of new methods and reagents for this transformation is still in demand.

The applications of bismuth compounds to organic transformations have been extensively investigated.[23] Recently, we introduced Bi(III) salts as efficient catalysts for the conversion of oxiranes to thiiranes,[24] deprotection of 1,1-diacetates,[25] alcoholysis, hydrolysis and acetolysis of epoxides,[26] deprotection of silyl ethers,[27] conversion of epoxides to 1,3-dioxolanes,[28] acetylation, benzoylation and formylation of alcohols and phenols.[29] As part of our ongoing program and interest in the introduction of new applications of Bi(III) salts, we became interested in developing a convenient method for conversion of thiocarbonyls to their carbonyl compounds. In this respect, we now report $Bi(NO_3)_3{\cdot}5H_2O$ as an efficient reagent for the deprotection of thioamides and thioureas (Scheme 1).[30]

Bismuth(III) nitrate pentahydrate is a commercially available reagent and requires no special handling. Several solvents including acetonitrile, dichloromethane, chloroform, ether and *n*-hexane were investigated during the course of this study; the best results were achieved using acetonitrile. As shown in Table 1, when a variety of primary, secondary and tertiary thioamides and thioureas were reacted with an equimolar amount of $Bi(NO_3)_3{\cdot}5H_2O$ in refluxing acetonitrile, the corresponding carbonyl compounds were obtained in excel-



Scheme 1.

Keywords: bismuth(III) nitrate pentahydrate; thiocarbonyls; carbonyl compounds.

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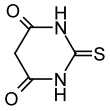
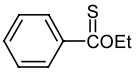
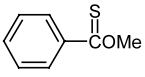
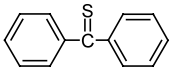
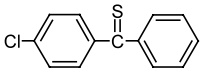
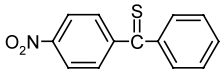
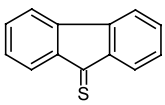
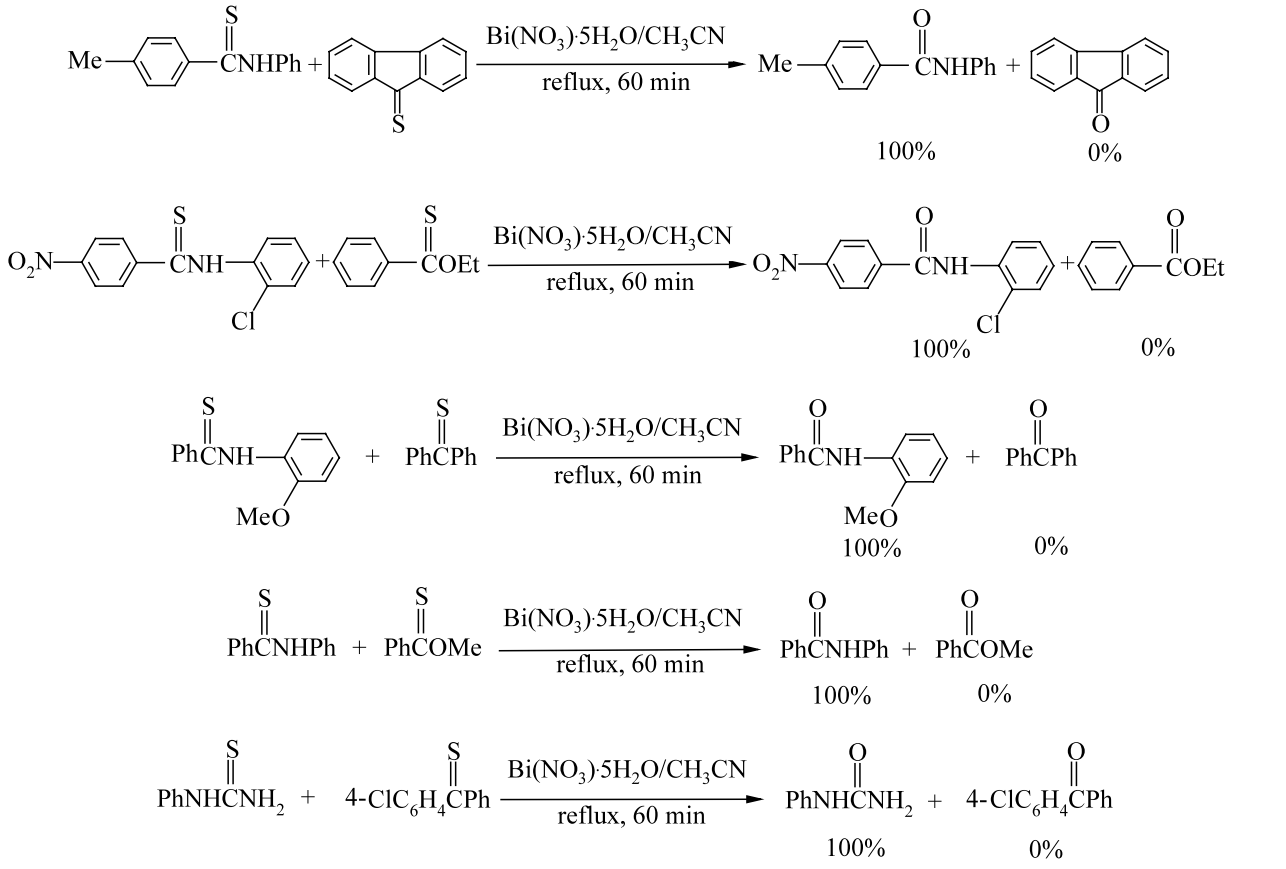
Table 1. Conversion of thiocarbonyls to carbonyl compounds with $Bi(NO_3)_3{\cdot}5H_2O$

Run	R^1	R^2	R^3	Time (min)	Yield [a,b] (%)
1	Me	H	H	10	97
2	NH_2	H	H	15	96
3	NH_2	NH_2	H	15	97
4	NH_2	Ph	H	20	98
5	PhNH	Ph	H	20	97
6	$H_2NC{=}S$ [c]	H	H	15	99
7	PhN=N	PhNH	H	20	96
8	Ph	Ph	H	5	98
9	Ph	$PhCH_2$	H	5	99
10	Ph	2-$MeOC_6H_4$	H	10	99
11	Ph	2-MeC_6H_4	H	5	96
12	Ph	4-$MeOC_6H_4$	H	10	92
13	Ph	4-MeC_6H_4	H	15	90
14	Ph	4-BrC_6H_4	H	15	92
15	Ph	4-$NO_2C_6H_4$	H	20	98
16	4-MeC_6H_4	Ph	H	10	99
17	4-$NO_2C_6H_4$	Ph	H	15	92
18	4-$NO_2C_6H_4$	2-$MeOC_6H_4$	H	15	98
19	4-$NO_2C_6H_4$	2-MeC_6H_4	H	15	95
20	4-$NO_2C_6H_4$	2-ClC_6H_4	H	15	99
21	2-ClC_6H_4	4-MeC_6H_4	H	15	93
22	4-MeC_6H_4	1-Naphthyl	H	15	98
23	Me	4-BrC_6H_4	H	10	99
24	Me	4-$NO_2C_6H_4$	H	10	98
25	3,5-$(NO_2)_2C_6H_3$	Ph	H	10	99
26	3,5-$(NO_2)_2C_6H_3$	2-MeC_6H_4	H	10	92
27	Me	Ph	Me	10	98
28	4-$NO_2C_6H_4$	Ph	Me	10	95
29	3,5-$(NO_2)_2C_6H_3$	Me	Me	15	99
30	3,5-$(NO_2)_2C_6H_3$	Et	Et	15	91
31				15	94
32				60	25
33				60	27
34				60	22
35				60	18
36				60	20
37				60	15

[a] All of the products were characterized by comparison of their spectral and physical data with those of authentic samples.
[b] Isolated yields.
[c] Oxamide was obtained from the reaction mixture.



Scheme 2.

lent yields (entries 1–31). However, under the same reaction conditions thiono esters and thioketones are resistant towards deprotection with this reagent and the corresponding carbonyl compounds were obtained in relatively poor yields (entries 32–37).

We have also investigated the chemoselectivity of this method and the results are shown in Scheme 2. As can be seen, thioamides and thioureas are selectively converted to their oxo derivatives in the presence of thiono esters or thioketones. This is a noteworthy feature of the above protocol and represents a useful practical achievement in such deprotection reactions.

In conclusion, this work demonstrates a new, useful and selective method for deprotection of thioamides and thioureas. The advantages include excellent yields, short reaction times and the use of a commercially available, inexpensive, crystalline solid and relatively non-toxic reagent.

Acknowledgements

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30. General procedure: In a round-bottomed flask (50 mL) equipped with a magnetic stirrer and a condenser, a solution of substrate (1 mmol) in CH_3CN (10 mL) was prepared. $Bi(NO_3)_3{\cdot}5H_2O$ (1 mmol) was added to the solution and the mixture was refluxed for the appropriate time according to Table 1. The progress of the reaction was followed 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 resulting crude material was either recrystallized from $EtOH/H_2O$ or subjected to column chromatography to afford the pure product (Table 1).