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A convenient and inexpensive method for conversion of thioamide compounds to their oxo derivatives using acidified iodine monochloride

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A series of thioamides are transformed to their corresponding oxo analogues in excellent yields with acidified iodine monochloride in acetonitrile at room temperature.

Keywords: thioamides; transformation; acidified iodine monochloride; oxidations; amide

1. Introduction

Functional group manipulations are of paramount importance to synthetic organic chemists and hence, the development of the novel transformations still remains of great interest. The conversion of thiocarbonyl compounds to their oxygen analogues has attracted considerable attention. Amides are valuable chemical intermediates in some organic reactions. They can be hydrolyzed to carboxylic acids, dehydrated to nitriles and degraded to amines in Hofmann rearrangement (*1*). Different methods and reagents such as *t*-butyl hypochlorite (*2*), diaryl selenoxide (*3*), dimethyl selenoxide (*4*), diaryl telluroxide (*5*), benzeneseleninic anhydride (*6*), singlet-oxygen (*7*), thiophosgene (*8*), sodiumperoxide (*9*), dimethyl sulfoxide/iodine (*10*), *m*-chloroperbenzoic acid (*11*), $NOBF_4$ (*12*), *N*-nitrosamines (*13*), soft NO^+ species (*14*), trifluoroacetic anhydride (*15*), clayfen (*16*), *p*-nitrobenzaldehyde/TMSOTf (*17*), 2-nitrobenzenesulfonyl chloride/potassium superoxide (*18*), manganese dioxide (*19*), clayfen or clayan/MW (*20*), Caro's acid supported on silica gel (*21*), ceric ammonium nitrate (*22*), oxone (*23*), $(n\text{-}BuPPh_3)_2S_2O_8$ (*24*), $(n\text{-}BuPPh_3)_2Cr_2O_7$ (*25*), 3-carboxypyridinium and 2,2′-bipyridinium chlorochromates (*26*), tetrabutylammonium periodate (*27*) and O_2/Cu (*28*) have been reported for the deprotection of thiocarbonyl compounds to their oxygen analogues.

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However, most of these reagents suffer from at least one of the disadvantages such as long reaction time, no selectivity, tedious work-up procedure, cost of preparation and low product yields. Furthermore, some of these methods are not suitable for deprotection of primary thioamides. Therefore, the introduction of new methods and reagents for this transformation is still required.

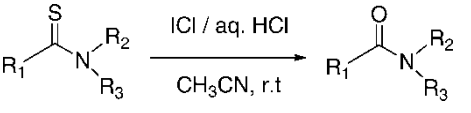
Iodine monochloride (ICl) is a good iodinating reagent and has two crystalline forms, α and β. In both structures, there are non-planner chains of ICl molecules in zig-zag formation (*29*).

ICl is a versatile reagent for halogenation of pyrazoles (*30*), activated aromatics (*31*), silyl-enol ethers and indoles (*32*), iodo-deboronation of hindered alkenyl boronate esters (*33*), oxidation of urazoles (*34*) and 1,4-dihydropyridines (*35*).

This compound is also applied for investigation of charge transfer complex formation with carbonyl and thiocarbonyl compounds (*36*) or benzene (*37*).

2. Results and discussion

In continuation of our ongoing research program (*35*), we wish to report mild and efficient conversion of thioamides into the corresponding oxo compounds by the use of ICl. As shown in Scheme 1, various thioamides were subjected with ICl to afford to corresponding amides in excellent yields at room temperature.



Scheme 1. Transformation of thioamides to corresponding amides.

For the choice of the reaction media, different solvents were investigated for the conversion of *N*-thiobenzoylaniline to *N*-benzoylaniline as typical substrate using ICl/aq. HCl at room temperature. As shown in Table 1, among the studied solvents, CH_3CN was found to be a suitable solvent because the higher amide derivative was observed. In the absence of acid, the conversion of thioamides was decreased to 10–40% yields. By employing 1 molar equivalent of the reagent in CH_3CN and 2 molar HCl aqueous solution, amide was obtained in 95% yield after 20 min. These conditions were applied for the conversion of other thioamides into their corresponding amides. The results are summarized in Table 1.

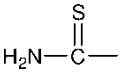
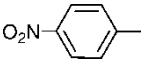
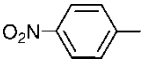
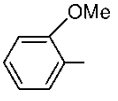
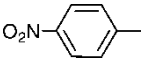
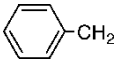
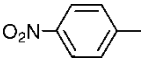
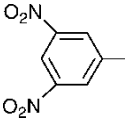
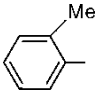
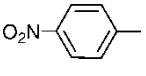
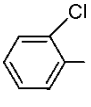
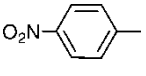
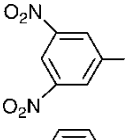
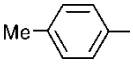
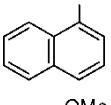
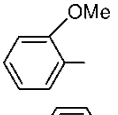
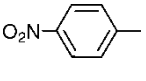
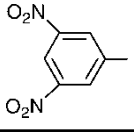
As shown in Table 2, a variety of thioamides (primary, secondary and tertiary) were treated with ICl in the presence of aqueous HCl in acetonitrile to afford the corresponding carbonyl compounds

Table 1. Conversion of *N*-thiobenzoyl aniline to corresponding amide with ICl/aq. HCl in different solvents at room temperature.

Solvent	ICl (mmol)	Time (min)	Yield(%)[a]
CCl_4	1	60	10
CH_3COCH_3	1	60	10
CH_3OH	1	60	15
CH_3CH_2OH	1	60	15
$CHCl_3$	1	100	5
CH_2Cl_2	1	100	5
CH_3CN	1	20	95
CH_3CN	0.5	60	70
CH_3CN	0.25	90	40

Note: [a]Isolated yields.

Table 2. Transformation of thioamide derivatives to the corresponding amides with ICl/aq. HCl in acetonitrile.

Entry	R_1	R_2	R_3	Time (min)	Yields[a] (%)	Mp found	(°C) reported (*38*)
1		H	H	20	96	299	>300
2			H	20	95	160	163
3			H	30	93	153	155
4			H	35	96	146	148
5			Me	60	90	105–107	107
6			H	40	92	151	152–153
7	ME		H	15	95	215	216
8			H	30	94	239–240	241
9			H	20	95	159	160
10			H	35	94	210	211
11		Et	Et	60	90	87	89–90
12			H	30	92	170	173
13			H	40	94	59–61	60
14			H	40	92	200	199
15		Me	Me	60	90	128	127–130

Note: [a]Isolated yields.

Table 3. Comparison of some of our results with those reported in the literature.

Entry[a]	A[b]	B	C	D	E
1	96/20	85/180	85/10	84/40	93/30
2	95/20	–	90/15	81/80	95/30
3	93/30	–	78/25	–	93/55
5	90/60	90/180	90/25	–	94/10
7	95/15	–	95/20	–	–
10	94/35	–	90/30	–	92/70
12	92/30	–	90/30	–	95/20

Notes: Values refer to yield (%)/time (min) ratios.
[a]The entries refer to those in Table 2.
[b]A: Our method; B: Ag_2CO_3/Celite, CH_3CN, r.t. (*39*); C: oxone/solid phase (*23*b); D: n-$Bu_4N^+IO_4^-$/CH_2Cl_2, r.t. (*27*); E: (n-$BuPPh_3$)Cr_2O_7/CH_3CN, reflux (*25*).

in excellent yields at room temperature. In the case of thioketones such as thiocyclohexanone, thiobenzophenone or 3-thiopentanone, no reaction was observed under these conditions.

To show the utility of the method, large scale deprotection of some thioamides to their corresponding amides was also investigated in a 30 mmol scale. The results were comparable with those of small scale experiments. Therefore, it seems that this method is also applicable for operation on large scale desulfurization of thioamides.

With regard to the literature, the proposed mechanism includes a nucleophilic attack of sulfur atom of thioamide to I–Cl and then a nucleophilic attack of water to thiocarbonyl group to generate corresponding oxo analog. We suggest that HCl raises the ionic strength of organic reaction media. Higher ionic strength leads to more polarizability of the I–Cl bond in the reaction conditions and therefore the nucleophilic attack of thioamide to I–Cl is facilitated in shorter reaction times with respect to one in the absence of HCl.

In order to show the ability of our method in comparison with previous reports, some of our results have been summarized in Table 3. As shown, the yield/time ratios of the present method are better or comparable with others.

In conclusion, we have developed an efficient procedure for the conversion of thioamides to their carbonyl compounds using ICl/aq. HCl in acetonitrile, as a simple and inexpensive reagent at room temperature. The mild reaction condition, appropriate reaction times, high product yields and easy work-up are some advantages of the method.

3. Experimental

All of the products were identified by the comparison of their physical and spectral data with those of authentic samples. The starting thioamides were prepared according to described procedures (*40*, *41*).

Caution: Iodine monochloride is hazardous. Weighting of it should be performed under high ventilation. It is recommended that its fresh stock solution in reaction solvent be prepared and used.

3.1. *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 (5 mL) and aqueous HCl (5 mL) was treated with ICl (1 mmol) and the reaction mixture was stirred at the room temperature for the time indicated in Table 1. The progress of the reaction was monitored by TLC (eluent: CCl_4/EtOAc: 10/1). After completion of the reaction, saturated $NaHCO_3$ was added to the reaction mixture. The crude product was extracted by diethyl

ether (2×10 mL). The organic layer was separated and dried by anhydrous Na_2SO_4. 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. Selective spectroscopic data of *N*-methyl-*N*-(4-nitrobenzoyl) aniline (**5**): IR (KBr): 1650, 1105, 1355, 1500, 1526, 1605, 3078 cm^{-1};^{1}H-NMR ($CDCl_3$ 400 MHz): δ 3.31 (s, 3H), 6.83–6.84 (d, 2H), 6.99–7.04 (m, 1H), 7.07–7.08 (m, 2H), 7.24–7.26 (d, 2H), 7.82–7.84 (d, 2H); ^{13}C-NMR($CDCl_3$): δ 38.31, 123.04, 126.96, 127.37, 129.57, 142,17, 143.81, 147.96, 168.21.

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