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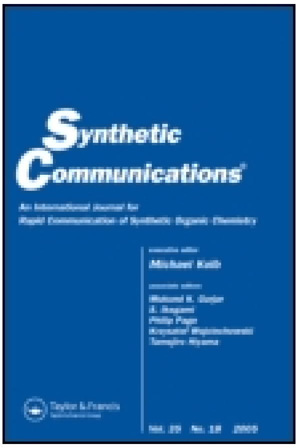

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Metal-Free, One-Pot Oxidative Conversion of Aldehydes to Primary Thioamides in Aqueous Media

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METAL-FREE, ONE-POT OXIDATIVE CONVERSION OF ALDEHYDES TO PRIMARY THIOAMIDES IN AQUEOUS MEDIA

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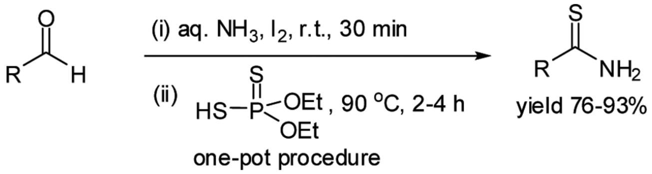
Green Synthesis Laboratory, Department of Chemistry, University of Allahabad, Allahabad, India

GRAPHICAL ABSTRACT



Abstract *One-pot tandem reactions of a variety of aldehydes with aqueous ammonia, molecular iodine, and O,O-diethyl dithiophosphoric acid readily afford the corresponding primary thioamides. This is an inexpensive, practical, and metal-free way of accessing various thioamides from aldehydes in aqueous media. The pure products are obtained simply by filtration followed by successive washing with aqueous sodium thiosulfate and water.*

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *for the following free supplemental resource(s): Full experimental and spectral details.]*

Keywords Aldehydes; deoxygenation; green chemistry; nitriles; *O,O*-diethyl dithiophosphopric acid; thioamides

INTRODUCTION

Thioamides and their derivatives have attracted considerable attention because of their utility in the synthesis of a variety of biologically and pharmaceutically relevant heterocycles such as thiazoles and thiazolines,[1] betaines,[2] mesoionic rhodanines,[3] and other hetrocycles.[4] In particular, they are useful building blocks in the Hantzsch thiazole synthesis for the preparation of a wide variety of substrates.[5] Some thioamide derivatives have been reported to exhibit potent activity against parasitic nematodes,[6] antitubercular activity,[7] iminosupressive activity, DHODH inhibitory properties,[8] and opioid activity at m- and d-recepters.[9] A series of thioamides has also been found to possess strong HIV-1 reverse transcriptase

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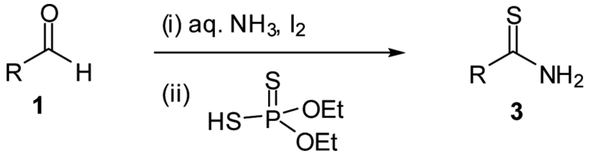


Scheme 1. One-pot oxidative conversion of aldehydes to thioamides.

inhibitory action.[10] Thioamides are used in rubber vulcanization and as boosters or as inhibitors of metal corrosion.[11]

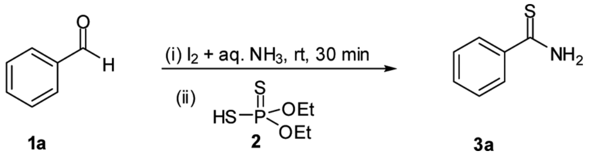
Many methods have been reported in the literature for the preparation of primary thioamides. These methods include (i) conversion of aldehydes to oximes and then to thioamides using reagents such as $PSCl_3$,[12] $(NH_4)_2S$ with $TiCl_3OTf$-[bmim]Br,[13] and *O,O*-diethyl dithiophosphoric acid;[14] (ii) conversion of amides to thioamides using Lawesson's reagents,[15] $(NH_4)_2S$ in Tf_2O at −40 °C,[16] P_4S_{10}[17] and $PSCl_3$;[18] (iii) conversion of nitriles to thioamides using alkali metal hydrogen sulfide or $(NH_4)_2S$ under pressure in a closed reactor or using $(P_4S_{11})Na_2$;[19] (iv) condensation of aldehydes and amines in the presence of S/Na_2S at high temperature (120 °C),[20] and carboxylic acids and amines in the presence of ammonium phosphorodithioate.[21]

To the best of our knowledge, only one method is known for the one-pot conversion of aldehydes to primary thioamides without oximation.[19b] However, this method suffers from several drawbacks: the reaction is performed in a sealed vessel (under pressure), requires high temperature (160–180 °C), gives poor yields (36–46%) of primary thioamides, and limited examples (only four) are available. In view of overcoming these drawbacks and filling the gap in the literature for a convenient one-pot synthesis of primary thioamides from aldehydes without oximation, we hypothesized that aldehydes could be converted to the corresponding primary thioamides through nitriles in a one-pot procedure as depicted in Scheme 1. To realize this hypothesis, we required reagents that would efficiently convert aldehydes to nitriles and in turn to primary thioamides ($RCHO \rightarrow RCN \rightarrow RCSNH_2$) without interfering with each other. For the first step ($RCHO \rightarrow RCN$), we selected aqueous NH_3/I_2[22] and for the second step ($RCN \rightarrow CSNH_2$), *O,O*-diethyl dithiophosphoric acid (**2**) was picked up, which has been previously used by us in various deoxygenative sulfurization–cyclization reactions.[23] To our delight, these reagents worked well for the envisaged one-pot conversion of aldehydes **1** to the corresponding thioamides **3** in aqueous media (Scheme 1).

RESULTS AND DISCUSSION

We started our study with the model reaction of aldehyde **1a**, iodine, aqueous ammonia, and *O,O*-diethyl dithiophosphoric acid (**2**) in aqueous media. The reaction mixture was stirred at rt for 30 min followed by stirring at 90 °C for 2 h to afford the desired primary thioamide **3a** in 85% isolated yield (Table 1, entry 1). Although water qualifies as an efficient green solvent for the present reaction, we also performed the reaction in various organic solvents for comparison purposes. Obviously, among the tested solvents, water was the best not only in view of the environmental concerns but also in terms of the yield and reaction time (Table 1).

Table 1. One-pot conversion of benzaldehydes to thiobenzamides in various solvents[a]



Entry	Solvent	Temp. (°C)[b]	Time (h)[c]	Conv. (%)[d]	Select. (%)[e]	Yield (%)[f]
1	H_2O	90	2	91	97	85
2	H_2O	Reflux	2	91	96	84
3	H_2O	75	2	83	98	78
4	Dioxane	90	3	84	97	78
5	Dioxane	Reflux	3	85	96	78
6	THF	Reflux	3	80	98	76
7	DCE	Reflux	4	75	98	70
8	Toluene	90	4	69	98	65
9	Toluene	Reflux	4	70	96	64
10	EtOH	Reflux	3	86	97	80

[a] Reaction conditions: **1a** (1.5 mmol), I_2 (1.6 mmol), 10 mL of 28% aq. NH_3, and *O,O*-diethyl dithiophosphoric acid (**2**) (1.5 mL).

[b] Temperature for step (ii).

[c] Time for step (ii).

[d] Conversion (%) of benzaldehyde (**1a**) as determined by GC analysis.

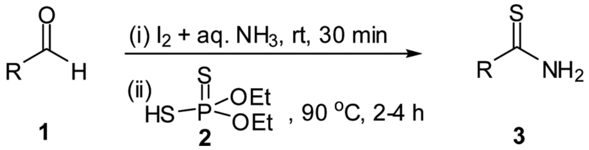
[e] Selectivity (%) for thioamide **3a**; the other side product was benzamide.

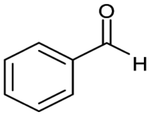
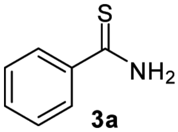
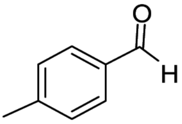
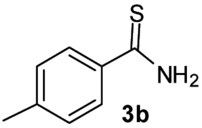
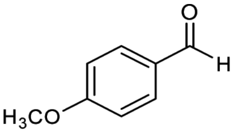
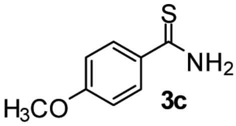
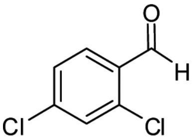
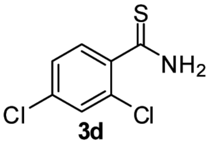
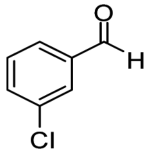
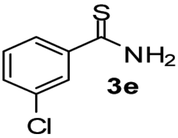
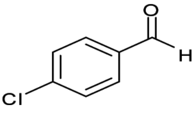
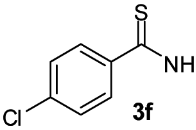
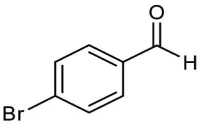
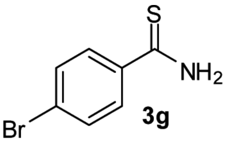
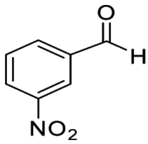
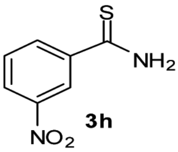
[f] Yield of isolated and purifide product **3a**.

Next, we examined the generality and substrate scope (Table 2). A wide range of aldehydes, including aromatic, heterocyclic, and aliphatic, were converted into the corresponding primary thioamides in good to excellent yields (76–93%). In the case of aromatic aldehydes both electron-donating and electron-withdrawing groups were tolerated. In general, the presence of an electron-withdrawing group in the substrates required longer reaction time and afforded lower yields of the corresponding thioamides **3** as compared to those bearing an electron-donating group (Table 2, entries 2 and 3 compared to entries 4–11 and 14). This might to be attributed to the difficulty in protonation of the corresponding nitriles **5** with dithiophosphoric acid **2** (Scheme 2) because aromatic aldehydes containing either electron-donating or electron-withdrawing subtituents have already been reported to give nitriles **5** in comparable yields under similar reaction conditions.[24]

On the basis of these experimental results and the literature precedents,[12,21,22,24] a plausible mechanism for the conversion of aldehydes **1** to primary thioamides **3** is depicted in Scheme 2. Aldehydes **1** on condensation with NH_3 form aldimines **4**, which are oxidized with molecular iodine to nitriles **5**. *O,O*-Diethyl dihiophosphoric acid (**2**) protonates nitriles **5** to generate nitrilium ions **6**, which combine with the nucleophile **7** present in the reaction mixture to form dithiophosphoric esters **8**. The hydrolysis of **8** affords primary thioamides **3**. Alternatively, nitrilium ions **6** could combine with water to form primary amides **9** (Table 2, footnote d), which react with **2** to give thioamides **3** via **10** (Scheme 2).

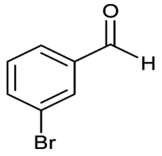
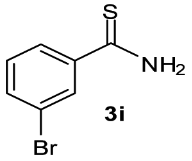
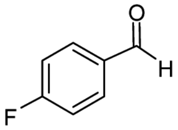
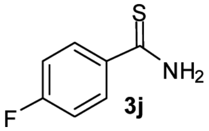
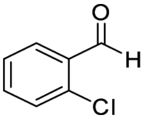
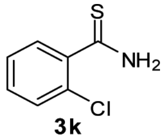
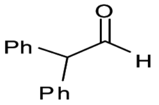
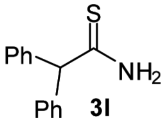
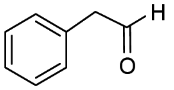
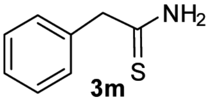
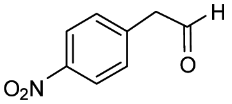
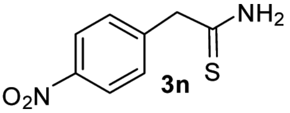
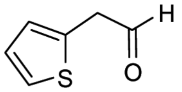
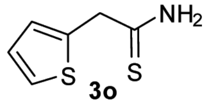
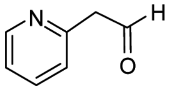
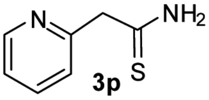
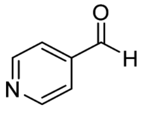
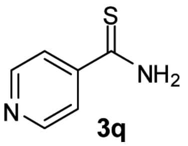
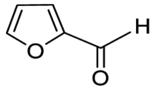
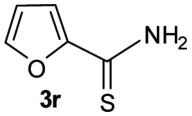
Table 2. One-pot conversion of aldehydes to thioamides in aqueous media[a]



Entry	Aldehyde **1**	Product **3**[b]	Time (h)	Conversion (%)[c]	Select. (%)[d]	Yield (%)[e]
1		 **3a**	2	91	97	85
2		 **3b**	2	95	97	89
3		 **3c**	2	97	98	93
4		 **3d**	4	80	98	76
5		 **3e**	3	90	97	84
6		 **3f**	4	87	96	81
7		 **3g**	3	88	97	82
8		 **3h**	3	82	98	80

(*Continued*)

Table 2. Continued

Entry	Aldehyde **1**	Product **3**[b]	Time (h)	Conversion (%)[c]	Select. (%)[d]	Yield (%)[e]
9		 **3i**	2	90	96	83
10		 **3j**	3	89	92	78
11		 **3k**	3	83	98	79
12		 **3l**	2	93	95	86
13		 **3m**	2	92	93	83
14		 **3n**	4	84	94	76
15		 **3o**	3	87	96	80
16		 **3p**	4	88	92	78
17		 **3q**	4	84	98	80
18		 **3r**	3	89	96	83

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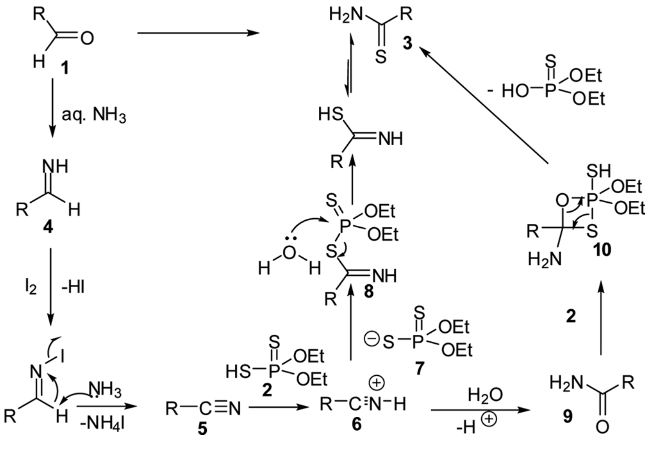
[a] For general procedure, see Experimental.

[b] All the products are known compounds and were characterized by comparison of their mp and spectral data with those reported in the literature (Table 3). [12,19j,21,25]

[c] Conversion (%) as determined by GC analysis.

[d] Selectivity (%) for thioamide **3**; the other side product was the corresponding amide.

[e] Yield of isolated and purified product **3**..



Scheme 2. Plausible mechanistic pathway for oxidative conversion of aldehydes to thioamides.

EXPERIMENTAL

Melting points were determined by open glass capillary method and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker AVII 400 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal reference. Mass spectrometry (MS) experiments were performed on a double-focusing MS spectrometer. All chemicals used were reagent grade and were used as received without further purification. Thin-layer chromatography (TLC) was performed using silica gel GF254 (Merck) plates.

General Procedure for the One-Pot Synthesis of Primary Thioamides 3a–3r

A mixture of benzaldehyde **1** (1.5 mmol) and iodine (1.6 mmol) in ammonia water (10 mL of 28% solution) was stirred at room temperature for 30 min. The dark reaction mixture faded in color at the end of reaction. The excess of ammonia was removed by stirring at 90 °C, and the gas was trapped in water. Then, *O,O*-diethyl dithiophosphoric acid (**2**) (1.5 mmol) was added and the reaction mixture was stirred at 90 °C for 2–4 h (Table 2, entry 1). After completion of the reaction (monitored by TLC), the mixture was cooled to rt. The product thus precipitated was filtered, washed with aqueous sodium thiosulfate solution followed by water, and dried under reduced pressure to give pure primary thioamides **3** (Table 2, entry 1). All products are known compounds and were characterized by comparison of mp and spectral data with those reported in the literature.[12,19j,21,25]

Benzothioamide (3a)[25a]

Pale yellow solid; yield: mp 113–115 °C [lit. mp 113–114 °C]. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.91$ (br s, 1H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.53 (t, $J = 8.0$ Hz, Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 2H), 7.29 (br s, 1H). HRMS (EI): calcd. for C_7H_7NS 137.0299; found 137.0298.

CONCLUSION

In summary, we have developed an efficient one-pot procedure for the conversion of aldehydes to the corresponding primary thioamides in aqueous media. The protocol involves tandem reactions of aldehydes with aqueous ammonia, molecular iodine, and *O,O*-diethyl dithiophosphoric acid to afford primary thioamides in good to excellent yields under environmentally benign conditions. The reagent *O,O*-diethyl dithiophosphoric acid acts both as an acid and a source of sulfur. We believe that the present operationally simple method would be a practical alternative to the existing procedures for the synthesis of primary thioamides.

SUPPORTING INFORMATION

Full experimental detail and ^{1}H NMR and HRMS data can be found via the Supplementary Content section of this article's Web page.

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