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Dithiocarbamate as an efficient intermediate for the synthesis of 2-amino-1,3,4-thiadiazoles in water

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ABSTRACT

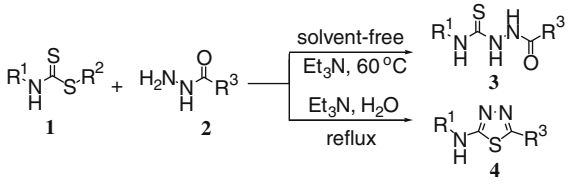
A new and facile protocol for the synthesis of 2-amino-1,3,4-thiadiazoles in water is described. Reaction of acid hydrazides with easily prepared dithiocarbamates gives the corresponding thiadiazoles in moderate to excellent yields. 2-Amino-1,3,4-oxadiazoles were not observed as side products using this procedure.

The synthesis of organic molecules via green, mild, and simple procedures is currently receiving considerable attention. Also, reducing or eliminating the use and generation of hazardous substances is a goal of green chemistry. In this context, water is the preferred choice as a solvent. Reactions in aqueous media are generally environmentally safe, devoid of any carcinogenic effects, are simple to handle, cheaper to operate, and are especially important in industry.[1]

The development of efficient methods for the synthesis of 1,3,4-thiadiazoles has attracted significant interest. Substituted 1,3,4-thiadiazoles have become very useful compounds in medicine, agriculture, and in many fields of technology such as dyes,[2] lubricating compositions,[3] optically active liquid crystals,[4] photographic materials[5], and many others. Also, applications of 1,3,4-thiadiazoles in agriculture as herbicides,[6] fungicides[7], and bacteriocides[8] have been patented. Acetazolamide (acetazol), a carbonic anhydrase inhibitor launched in 1954, is a well-known drug based on the 1,3,4-thiadiazole ring.[9] Also, 1,3,4-thiadiazole derivatives have shown anti-inflammatory activity.[10]

A variety of synthetic methods for the preparation of 1,3,4-thiadiazoles have been reported. One of the most common procedures involves the cyclization of a 1,2-diacylhydrazine or its thia analog in the presence of a coupling agent such as $SOCl_2$ or $POCl_3$, and a strong mineral acid.[11] Several recent publications have reported milder cyclization methods using $(PhO)_2P(O)Cl$, Ph_3P, TMSCl, and Lawesson's reagent for the synthesis of 1,3,4-thiadiazoles.[12] There are many reports on the multi-step synthesis of thiadiazoles,[13] however, one-pot or one-step syntheses are rare. Varma and co-workers reported the first one-pot, one-step, solvent-free procedure for the synthesis of substituted 1,3,4-thiadiazoles using acid hydrazides and triethylorthoalkanoates in the presence of P_4S_{10}/Al_2O_3 under microwave irradiation.[14] Solid-phase synthesis of 2-amino-1,3,4-thiadiazole derivatives via selective, reagent-based cyclization of acyldithiocarbazate resins was reported by Gong.[12a] Also, Lau and co-workers reported the synthesis of 2-amino-1,3,4-thiadiazole derivatives via reaction of a thiosemicarbazide bound to a resin and an aldehyde, followed by cyclization of the resulting thiosemicarbazone with a solution of iron(III) chloride in dichloromethane/methanol.[15]

We recently reported several green, one-pot, and simple methods for the synthesis of dithiocarbamates from amines, CS_2, and different nucleophile acceptors, such as alkyl halides, activated olefins, and epoxides, under solvent-free and aqueous conditions.[16] In continuation of our interest in the synthesis of novel dithiocarbamates and the use of these intermediates in organic transformations,[17] we have focused our attention on the reaction of dithiocarbamate **1** with acid hydrazide **2** (Scheme 1). We found that compound **3** was the only product and no cyclization product was observed. Also, on refluxing the reaction mixture in high boiling point solvents such as benzene, toluene, and DMF, acyclic product **3** was formed. Surprisingly, we found that the reaction of the dithiocarbamate and acid hydrazide in the presence of triethylamine or pyridine in water and under reflux, afforded the substituted 2-amino-1,3,4-thiadiazole **4** in



Scheme 1. Reaction of dithiocarbamate **1** with acid hydrazide **2** in water and under solvent-free conditions.

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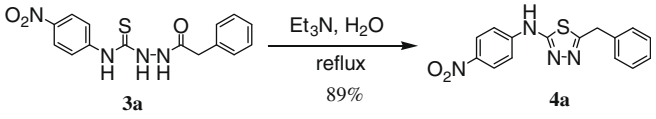
excellent yield. When the reaction was carried out at low temperature over a short reaction time, compound **3** was detected as a side product. No oxadiazole was observed as a by-product. After synthesizing the starting dithiocarbamates and acid hydrazides, optimization of the reaction conditions was achieved by varying the number of equivalents of dithiocarbamate, acid hydrazide, and triethylamine, the temperature and the solvent. We obtained excellent yields when one equivalent of each of dithiocarbamate and acid hydrazide in water was heated under reflux in the presence of 2 equiv of triethylamine.

Next, the scope and limitations of this process were explored using a wide range of acid hydrazides and dithiocarbamates. As shown in Table 1, dithiocarbamates derived from primary aliphatic and aromatic amines underwent the reaction in water to afford thiadiazoles **4** in moderate to excellent yields without using any cyclization promoters. Moderate to excellent yields were obtained with aliphatic and aromatic acid hydrazides. Optically active 1,3,4-thiadiazoles were synthesized by reaction of a chiral dithiocarbamate with acid hydrazides in moderate to excellent yields (Table 1, entries 21–25). The stereogenic center of these compounds remained intact and the ees were the same as those of the starting materials as shown by the use of a chiral shift reagent ($R/S \sim 98{:}2$). Also thiadiazoles, which are used in coordination chemistry, were synthesized from *ortho* hydroxy acid hydrazides in good yields (Table 1, entries 5, 8, 14, 17, and 25). Similarly, a 1,3,4-thiadiazole containing an adamantyl group was prepared in excellent yield (Table 1, entry 26). Reactions with dithiocarbamates derived from secondary amines were not possible. The structures of the products were elucidated from their IR, ^{1}H and ^{13}C NMR, and mass spectra. In DMSO-d_6, the ^{1}H NMR spectra showed broad peaks for the NH of the amine group at 10–13 ppm. In $CDCl_3$ this peak was shifted to 6–9 ppm. The ^{13}C NMR spectra clearly showed that the thiadiazole was the only product, the chemical shifts of C-2 at 151–154 ppm and C-5 at 168–172 ppm were in the ranges reported in the literature.[12a] Also mass spectrometry confirmed the molecular formula.

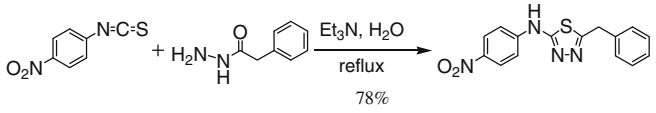
To show that the reaction occurs via intermediate **3a**, we performed the cyclization reaction with the freshly prepared thiosemicarbazide under the same reaction conditions. The 2-amino-1,3,4-thiadiazole **4a** was obtained in excellent yield (Scheme 2).

To investigate the efficiency of the reaction medium, we studied the reaction of an acid hydrazide with an isothiocyanate in the presence of water and triethylamine. The corresponding 2-amino-1,3,4-thiadiazole was obtained in high yield (Scheme 3).

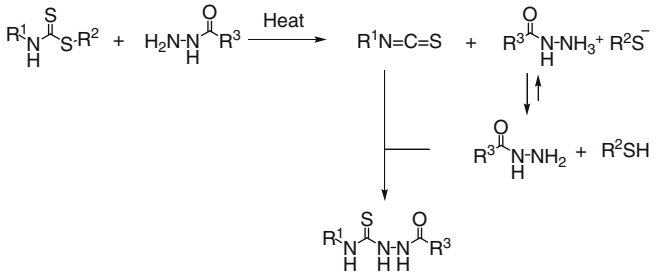
Scheme 4 shows a possible pathway for the reaction between the dithiocarbamate and acid hydrazide. It is thought that the reaction occurs by an elimination–addition mechanism, involving elimination of an alkylthiol with the formation of an isothiocyanate, which immediately undergoes addition to the acid hydrazide, to give a thiosemicarbazide. This mechanism also shows why dithiocarbamates prepared from secondary amines did not give the expected products.



Scheme 2. Synthesis of 2-amino-1,3,4-thiadiazole from thiosemicarbazide **3a** in water.

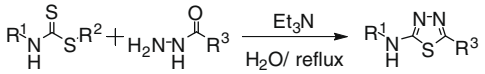


Scheme 3. Synthesis of a 2-amino-1,3,4-thiadiazole via reaction of an acid hydrazide with an isothiocyanate.



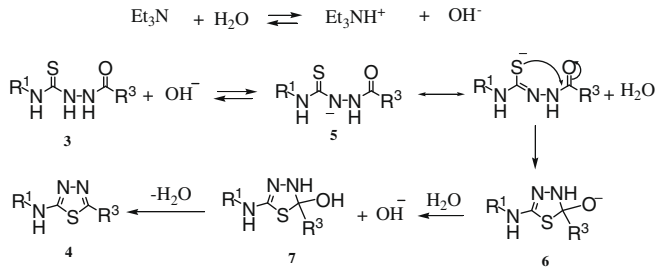
Scheme 4. Proposed mechanism for the synthesis of thiosemicarbazides.

Table 1
Synthesis of 5-substituted-2-amino-1,3,4-thiadiazoles using dithiocarbamates and acid hydrazides in water[18]



Entry	r^1	R^2	R^3	Yield[a,b,c] (%)	Entry	R^1	R^2	R^3	Yield (%)[a,b,c]
1	Ph	$-CH_2CH_2CN$	Ph	95[13g]	15	n-Bu	Et	4-Pyridine	68
2	Ph	$-CH_2CH_2CN$	$PhCH_2$	96	16	$PhCH_2$	Et	Ph	89[13g]
3	Ph	$-CH_2CH_2CN$	4-MeC_6H_4	92[13g]	17	$PhCH_2$	Et	2-HOC_6H_4	84
4	Ph	$-CH_2CH_2CN$	4-Pyridine	75[13]	18	$PhCH_2$	Et	4-MeC_6H_4	88
5	Ph	$-CH_2CH_2CN$	2-HOC_6H_4	68	19	$PhCH_2$	Et	4-Pyridine	88[13g]
6	3,4-$Cl_2C_6H_3$	Et	4-MeC_6H_4	97	20	$PhCH_2$	Et	$PhCH_2$	82
7	3,4-$Cl_2C_6H_3$	Et	Ph	89	21	(*R*)-1-Phenylethyl	Et	Ph	95[d]
8	3,4-$Cl_2C_6H_3$	Et	2-HOC_6H_4	51	22	(*R*)-1-Phenylethyl	Et	$PhCH_2$	90[d]
9	3,4-$Cl_2C_6H_3$	Et	4-Pyridine	71[13]	23	(*R*)-1-Phenylethyl	Et	4-MeC_6H_4	98[d]
10	3,4-$Cl_2C_6H_3$	Et	$PhCH_2$	91	24	(*R*)-1-Phenylethyl	Et	4-Pyridine	40[d]
11	*n*-Bu	Et	Ph	81	25	(R)-1-Phenylethyl	Et	2-HOC_6H_4	92[d]
12	*n*-Bu	Et	4-MeC_6H_4	88	26	Adamantyl	Et	4-MeC_6H_4	95
13	*n*-Bu	Et	$PhCH_2$	63					
14	*n*-Bu	Et	2-HOC_6H_4	80					

[a] Isolated yield.
[b] Reaction conditions: acid hydrazide (1 mmol), dithiocarbamate (1 mmol), Et_3N (2 mmol), and H_2O (4 mL).
[c] References are given for known compounds.
[d] Ees determined by GC and found to be the same as those of the starting materials ($R/S \sim 98{:}2$).



Scheme 5. Proposed mechanism for the synthesis of 2-amino-1,3,4-thiadiazoles in water.

A plausible mechanism for the synthesis of 2-amino-1,3,4-thiadiazoles is shown in Scheme 5. The reaction of triethylamine with water gave a mild basic media in which the thiosemicarbazide **3** can be converted into anion **5**, and then cyclization via nucleophilic attack of sulfur on the carbonyl group produces compound **7**. Aromatization of **7** proceeds with elimination of water. Water may play a dual role in this mechanism: producing the hydroxide ion and activating the carbonyl group via hydrogen bonding.

In conclusion, we have developed an efficient method for the synthesis of 1,3,4-thiadiazoles from readily prepared *S*-alkyl dithiocarbamates and acid hydrazides. We have also shown that substituted 2-amino-1,3,4-thiadiazoles can be synthesized by the reaction of dithiocarbamates prepared from aliphatic and aromatic primary amines and acid hydrazides in water in good to excellent yields. This protocol represents a one-pot, one-step, simple, and green procedure using mild reaction conditions, and has general applicability. It avoids hazardous organic solvents and toxic catalysts, especially in the cyclization step.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.11.100.

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18. *General Procedure for the one-pot reaction of acid hydrazides and dithiocarbamates in the presence of water*: In a round-bottomed flask equipped with a magnetic stirrer, acid hydrazide (1 mmol), dithiocarbamate (1 mmol), triethylamine (2 mmol), and H_2O (4 mL) were added. The mixture was heated at reflux for 18 h with vigorous stirring until conversion of the starting material was complete (TLC, EtOAc/petroleum ether; 1:2). The reaction mixture was cooled to room temperature and the product was collected by filtration, and washed with H_2O and hot petroleum ether to afford the pure product. For entries 2, 13, 19, 22, 23, and 25 in Table 1, extraction with EtOAc from aqueous media, washing with 1 N HCl, and evaporation of the solvent gave the product in high purity. All compounds were characterized on the basis of ^{1}H NMR, ^{13}C NMR, and mass spectroscopy. Table 1, entry 9: mp 232–235 °C. ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) = 7.35 (d, J = 5.8 Hz, 2H), 7.43 (dd, J = 8.5, 2.0 Hz, 1H), 7.82 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 2.1 Hz, 1H), 8.64 (d, J = 5.8 Hz, 2H), 14.1 (br s, 1H, -NH). ^{13}C NMR (125 MHz, DMSO-d_6): δ (ppm) = 122.9, 130.1, 131.9, 132.3, 132.5, 133.5, 133.8, 134.9, 149.1, 151.1, 170.0. Anal. Calcd for $C_{13}H_8Cl_2N_4S$: C, 48.29; H, 2.47; N, 17.33. Found: C, 47.95; H, 2.43; N, 17.42. Table 1, entry 11: mp 124–127 °C. ^{1}H NMR (500 MHz, acetone-d_6): δ (ppm) = 0.78 (t, J = 7.8 Hz, 3H), 1.19 (m, 2H), 1.62 (m, 2H), 4.10 (t, J = 7.8 Hz, 2H), 7.56–7.23 (m, 5H), 12.76 (br s, 1H, –NH). ^{13}C NMR (125 MHz, acetone-d_6): δ (ppm) = 12.5, 19.0, 30.9, 43.5, 128.1, 128.6, 130.0, 132.6, 151.4, 168.3. Anal. Calcd for $C_{12}H_{15}N_3S$: C, 61.80; H, 6.44; N, 18.02. Found: C, 61.64; H, 6.33; N, 17.89. Table 1, entry 12: ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.89 (t, J = 7.4 Hz, 3H), 1.29 (m, 2H), 1.73 (m, 2H), 2.47 (s, 3H), 4.12 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 7.9 Hz, 2H), 12.45 (br s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 13.9, 20.1, 21.9, 30.7, 45.0, 123.5, 128.9, 130.2, 141.8, 152.6, 167.8. MS (EI): m/z = 248 (20) $[M+1]^+$, 214 (100), 191 (58), 118 (33), 91 (28), 41 (27). Anal. Calcd for $C_{13}H_{17}N_3S$: C, 63.16; H, 6.88; N, 17.00. Found: C, 63.48; H, 6.91; N, 16.83. Table 1, entry 17: mp 178–181 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) = 5.34 (s, 2H), 6.85-7.38 (m, 9H), 9.32 (br s, 1H, –OH), 12.86 (br s, 1H, –NH). ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) = 47.8, 114.5, 116.9, 120.6, 127.5, 128.2, 128.9, 132.0, 134.6, 136.9, 151.1, 156.3, 169.6. Anal. Calcd for $C_{15}H_{13}N_3OS$: C, 63.60; H, 4.59; N, 14.84. Found: C, 63.18; H, 4.76; N, 15.15. Table 1, entry 18: mp 179–182 °C. ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) = 2.36 (s, 3H), 5.39 (s, 2H), 7.11–7.43 (m, 9H), 12.85 (br s, 1H, –NH). ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) = 21.3, 48.0, 124.5, 127.4, 128.2, 129.1, 129.3, 129.8, 137.1, 141.8, 152.9, 170.5. Anal. Calcd for $C_{16}H_{15}N_3S$: C, 68.33; H, 5.34; N, 14.95. Found: C, 68.67; H, 5.42; N, 14.73. Table 1, entry 19: mp 197–200 °C.) ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) = 5.57 (s, 2H), 7.14–7.32 (m, 5H), 7.55 (d, 2H, J = 5.8 Hz), 8.63 (d, 2H, J = 5.8 Hz), 13.14 (br s, 1H, –NH). ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) = 48.0, 123.1, 127.6, 128.5, 129.4, 134.6, 136.6, 150.6, 151.3, 171.1. Anal. Calcd for $C_{14}H_{12}N_4S$: C, 62.69; H, 4.48; N, 20.89. Found: C, 62.38; H, 4.62; N, 20.68. Table 1, entry 22: mp 118–121 °C. $[\alpha]_D^{20}$ 100.0 (c 1, $CHCl_3$), ^{1}H NMR (300 MHz, acetone-d_6): δ (ppm) = 1.67 (d, 3H, J = 7.3 Hz), 3.65 (s, 2H), 6.43 (1H, m), 6.95 (dd, 2H, J = 7.5, 2.0 Hz), 7.21–7.48 (m, 8H), 12.62 (br s, 1H, –NH). ^{13}C NMR (75 MHz, acetone-d_6): δ (ppm) = 14.3, 32.8, 53.6, 126.9, 127.4, 128.0, 128.9, 129.2, 129.5, 135.8, 139.7, 151.8, 169.7. Anal. Calcd for $C_{17}H_{17}N_3S$: C, 69.15; H, 5.76; N, 14.24. Found: C, 68.92; H, 5.32; N, 14.05.