Synthesis and reactivity of monothio-oxamides

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Dedicated to Professor B. A. Trofimov on the occasion of his 65th birthday

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Abstract

A convenient method has been developed for the synthesis of monothio-oxamides by the reaction of chloroacetamides with a previously prepared solution of elemental sulfur in amines. Oxalic acid derivatives and heterocyclic compounds were synthesized from the monothio-oxamides obtained.

Keywords: Chloroacetamides, sulfur, amines, monothio-oxamides, thiazoles, oxazoles

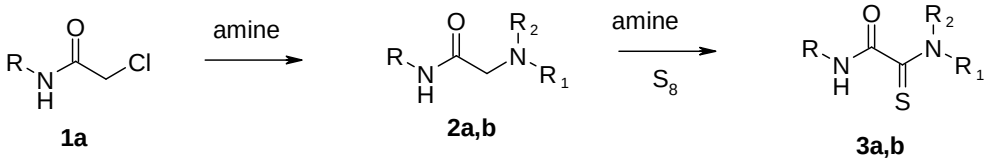
Introduction

The combination of amide species in close proximity in the same molecule of monothio-oxamides imparts unexpected properties to these compounds and makes them of considerable interest for the synthesis of various substances, including heterocyclic structures. Monothio-oxamide fragments are found in natural compounds,[1] and are under intensive study as biologically active substances.[2,3] Also, monothio-oxamides are of special interest as complex-forming structures.[4] However, despite their high synthetic potential, the chemistry of these compounds has been studied insufficiently prior to our studies,[5] mainly because convenient methods for their synthesis were unavailable.

Results and Discussion

In our opinion, the most attractive method for the synthesis of the monothio-oxamides is based on the reaction of chloroacetamides with elemental sulfur and amines. A few examples of this approach have been described in the literature,[6,7] but they have substantial disadvantages, one of the main being the necessity of prolonged heating of the reaction mixture. It is known that sulfur,

when heated, reacts with amines to form a complicated mixture of products,[8] which can impede the process of monothio-oxamide preparation. We have shown that the reaction under the conditions of the published procedure, in which elemental sulfur and the amine are simultaneously added to chloroacetamide, produces a large amount of α-aminoacetamides, which then react with sulfur only on prolonged heating.

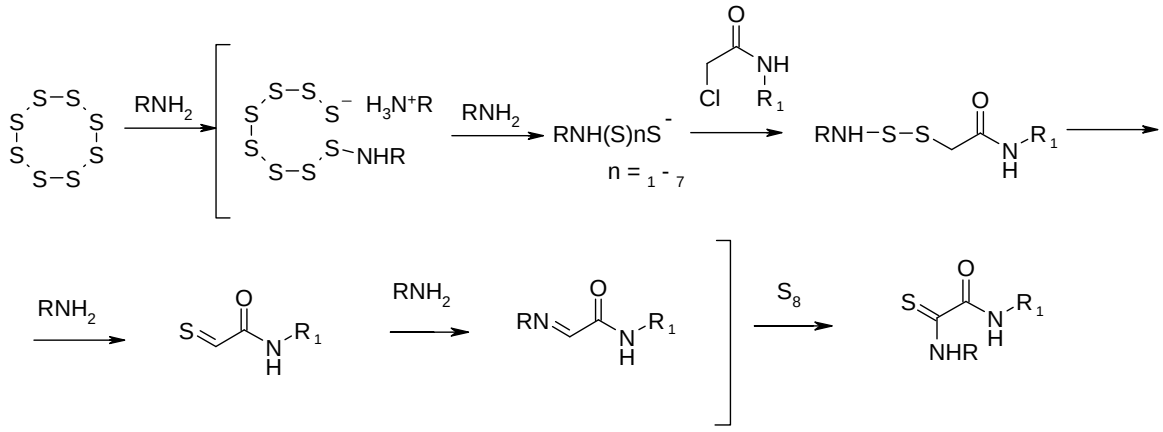


1a: R = Ph **2a**: R = Ph, R_1 = Bu, R_2 = H **3a**: R = Ph, R_1 =Bu, R_2 = H

2b: R = Ph, R_1,R_2 = $-(CH_2)_2-O-(CH_2)_2-$ **3b**: R = Ph, R_1,R_2 = $-(CH_2)_2-O-(CH_2)_2-$

Scheme 1

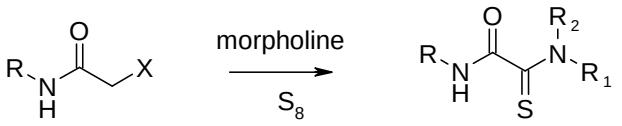
It is known[9] that when amines react with elemental sulfur for a rather long time, a considerable amount of polysulfide anion accumulates in the solution. These are formed by cleavage of the eight-membered cyclic molecule of elemental sulfur under the action of amines. It is most likely that at a sufficiently high concentration the polysulfide anions might react preferentially with chloroacetamides instead of the amines. The nucleophilic substitution of the chlorine atom affords the corresponding polysulfide, in which the amine molecules induce elimination of a proton simultaneously with the cleavage of the sulfide bond to form the thioaldehyde fragment. The reaction of thioaldehyde with amine affords the imine, which is oxidized further by sulfur to the corresponding thioamide fragment.



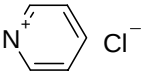
Scheme 2

We have established that monothio-oxamides are formed under mild conditions, in high yields, at room temperature using a solution of sulfur prepared previously in the corresponding amine (by stirring the components for 20–30 min). We have also studied the influence of solvents, the nature of the substituent in the α-position of the amides, and the nature of

substituents in the "acetamide" and "amine" components. The *S*-functionalization of chloroacetamides and their pyridinium salts occurs most smoothly.



1a-e **3b**

1a: R = Ph, X = Cl
1b: R = Ph, X = -SPh
1c: R = Ph, X = -SC(=O)NH_2
1d: R = Ph, X = -$SSCH_2C(=O)NHPh$
1e: R = Ph, X =  Cl^-

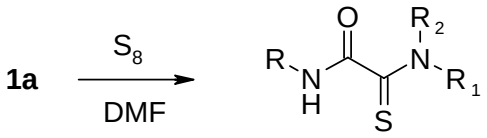
3b: R = Ph, R_1,R_2 = -$(CH_2)_2$-O-$(CH_2)_2$-

Scheme 3

Table 1. Yields of compound **3b** from acetamides **1a–e**

Acetamide	**1a**	**1b**	**1c**	**1d**	**1e**
Yield of **3b** (%)	92	12	23	7	89

The most convenient solvents for the reaction are DMF, pyridine, or the amine itself. We have shown that the mild conditions of the reactions make it possible to use DMF, while heating of a mixture of chloroacetamide and sulfur in DMF results in the corresponding monothio-oxamides containing the dimethylamino group in the thioamide fragment.

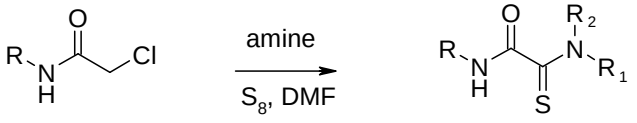


3c

3c: R = Ph, R_1 = R_2 = CH_3

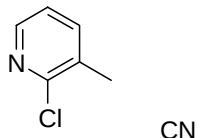
Scheme 4

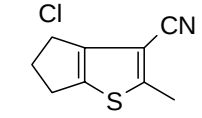
The nature of the substituent in the acetamide fragment has no substantial effect on the sulfurization of chloroacetamides. Acetamides containing electron-withdrawing and electron-donating substituents react almost in the same manner with the previously prepared solution of elemental sulfur in amides.



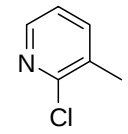
1a,f-j **3d-i**

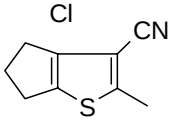
1f: R = 3,5-$(CF_3)_2C_6H_3$
1g: R = 3-$(NO_2)C_6H_4$
1h: R = 3,4-$(Cl)_2C_6H_3$





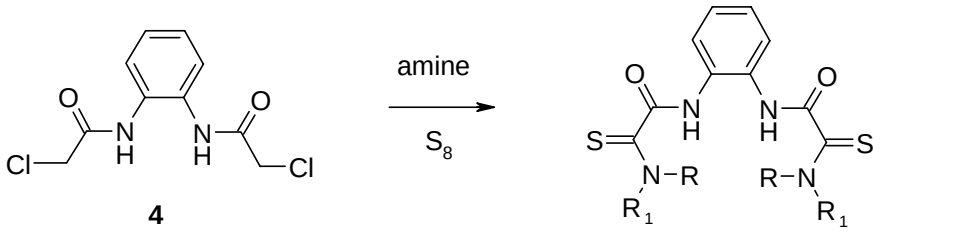
3d: R = Ph, R_1 = H, R_2 = -$CH_2CH_2CH_2NH$-(2-Cl-4-NO_2)C_6H_3
3e: R = 3,5-$(CF_3)_2C_6H_3$, $R_1 = R_2$ = Et
3f: R = 3-$(NO_2)C_6H_4$, R_1,R_2 = -$(CH_2)_5$-
3g: R = 3,4-$(Cl)_2C_6H_3$, R_1,R_2 = -$(CH_2)_5$-


3h: R = , R_1, R_2 = -$(CH_2)_2$-O-$(CH_2)_2$-


3i: R = , R_1, R_2 = -$(CH_2)_2$-O-$(CH_2)_2$-

Scheme 5

Our method also allows the synthesis of bis-substituted monothio-oxamides.

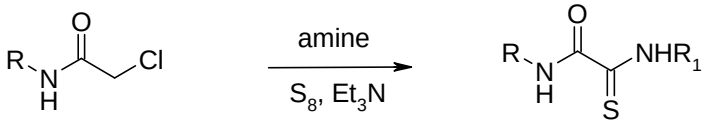


4 **5a,b**

5a: R = Ph, R_1 = H
5b: R,R_1 = -$(CH_2)_2$-O-$(CH_2)_2$-

Scheme 6

The effect of substituents in the "amine" component of the reaction is substantial. When anilines having a lower basicity than aliphatic amines are used, triethylamine should be added to the reaction mixture.



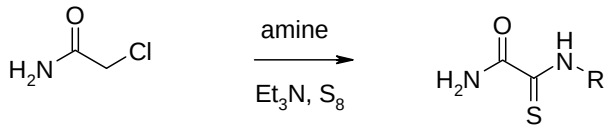
1a,k-n **6a-g**

1k: R = 2-(CN)C_6H_4
1l: R = 4-($CH_3OC(=O)$)C_6H_4
1m: R = 4-(Cl)C_6H_4
1n: R = H

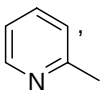
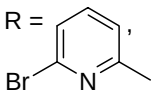
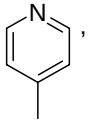
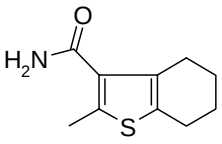
6a: R = Ph, R_1 = 4-($CH_3OC(=O)$)C_6H_4
6b: R = Ph, R_1 = 4-($CH_3C(=O)NH$)C_6H_4
6c: R = Ph, R_1 = 4-(Et_2N)C_6H_4
6d: R = 2-(CN)C_6H_4, R_1 = 4-(CH_3O)C_6H_4
6e: R = 4-(Cl)C_6H_4, R_1 = 4-(Cl)C_6H_4
6f: R = 4-($CH_3OC(=O)$)C_6H_4, R_1 = Ph
6g: R = H, R_1 = 1-naphthyl

Scheme 7

We have also demonstrated that heteroaromatic monothio-oxamides can be synthesized by the reaction of chloroacetamide with sulfur and heteroaromatic amines in the presence of triethylamine.

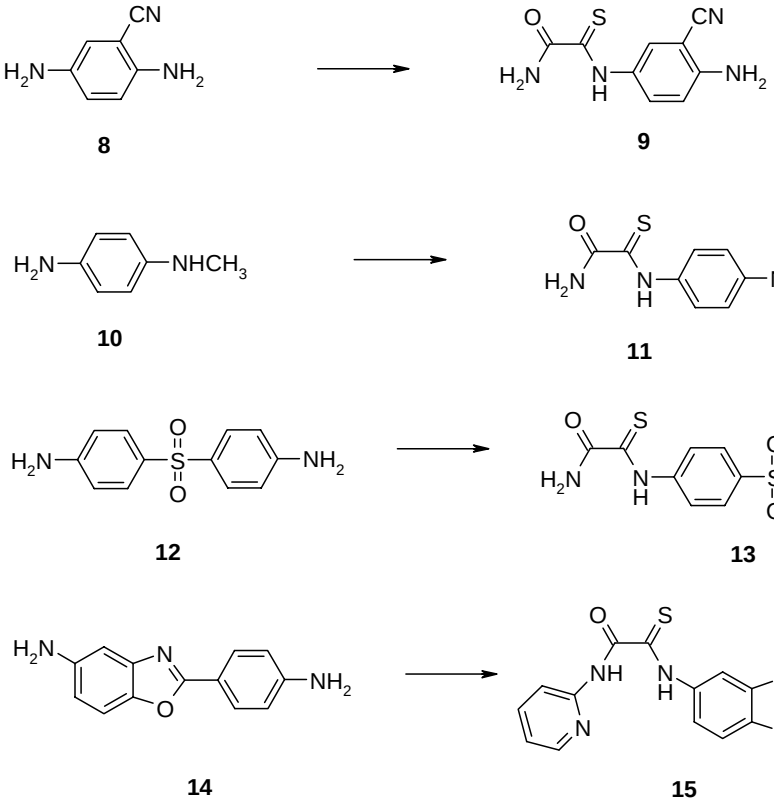


1n **7a-d**

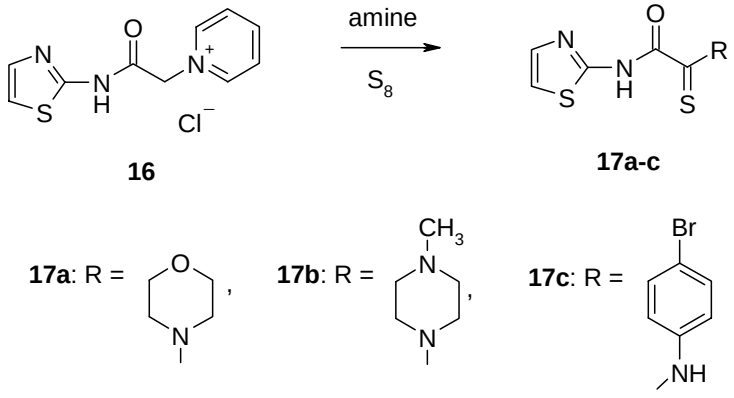
7a: R = 
7b: R = 
7c: R = 
7d: R = 

Scheme 8

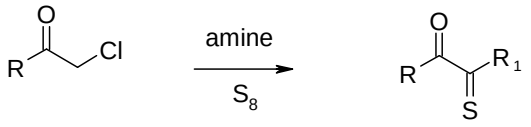
The use of aromatic, unlike aliphatic amines, makes it possible to perform the reaction at a single amino group. In several cases where the chloroacetamides did not react, it was necessary to use the corresponding pyridinium salts in the reactions with aromatic amines. This approach was useful for the synthesis of aminothiazole derivatives, as shown in Scheme 10.



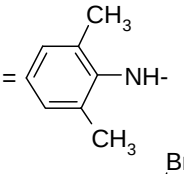
Scheme 9

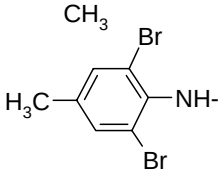


Scheme 10

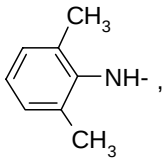
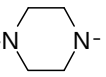


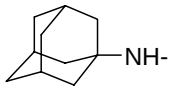
1a,n-q **18a-h**

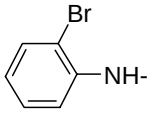
1o: R = 

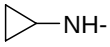
1p: R = 

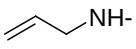
1q: R = 4-$(NO_2)C_6H_4NH$-

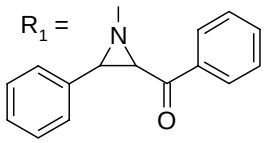
18a: R =  , R_1 = 

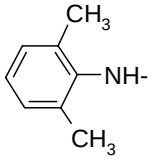
18b: R = PhNH-, R_1 = 

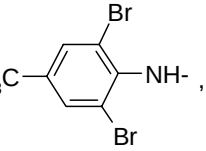
18c: R = H_2N- , R_1 = 

18d: R = PhNH-, R_1 = 

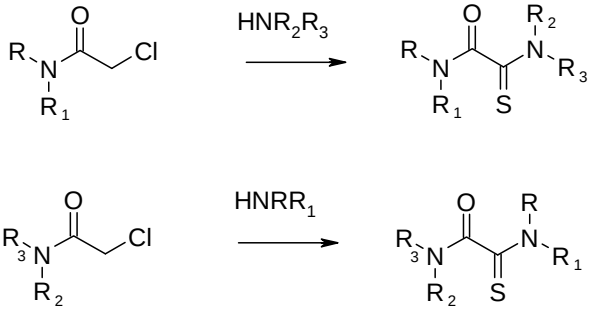
18e: R = PhNH-, R_1 = 

18f: R = H_2N- , R_1 = 

18g: R = 4-$(NO_2)C_6H_4NH$- , R_1 = 

18h: R = H_3C  , R_1 = $PhCH_2CH_2NH$-

Scheme 11

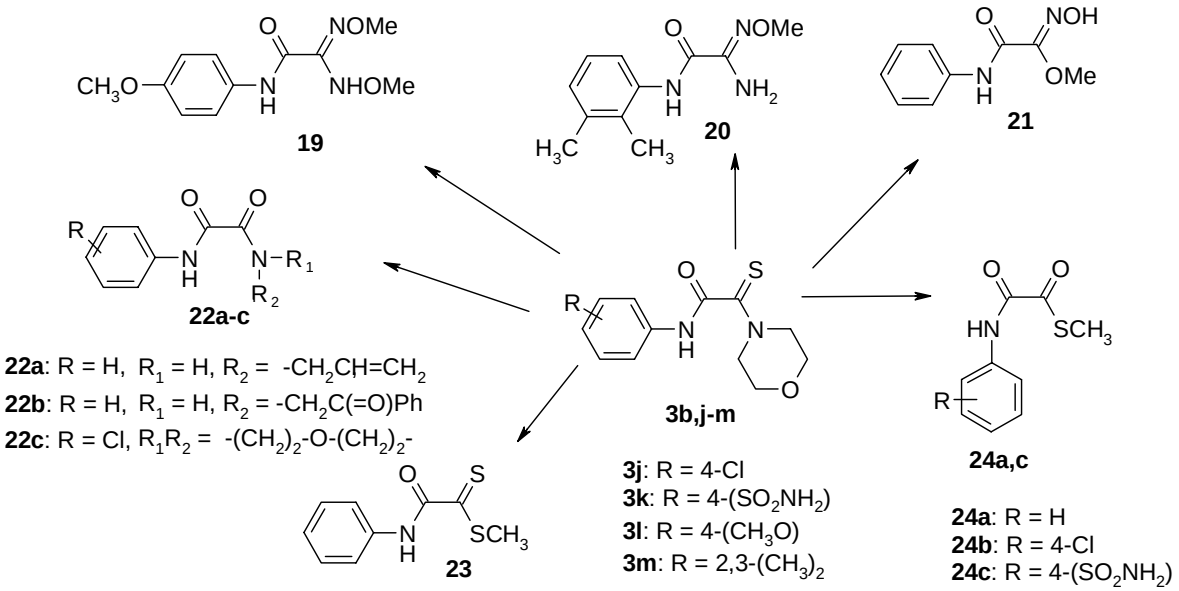


Scheme 12

Steric effects do not substantially affect the reaction, and this allows one to use hindered amines, including amino-adamantane. Unstable amines, for example cyclopropyl- and allyl-amines or aziridines, can be used in the reaction, owing to the mild conditions of the process.

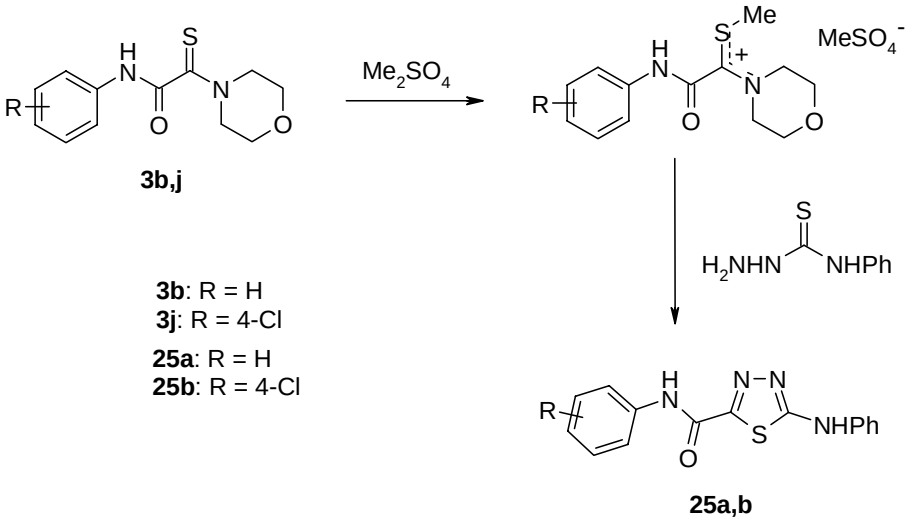
The method also allows the possibility of synthesizing isomers of monothio-oxamides, which can be obtained by the replacement of the "amine" and "acetamide" components of the reaction.

Thus, we have shown that the use of the previously prepared solution of sulfur in amines is a convenient method for the S-functionalization of α-chloroacetamides. The monothio-oxamides synthesized are convenient starting compounds for syntheses of various oxalic acid derivatives.



Scheme 13

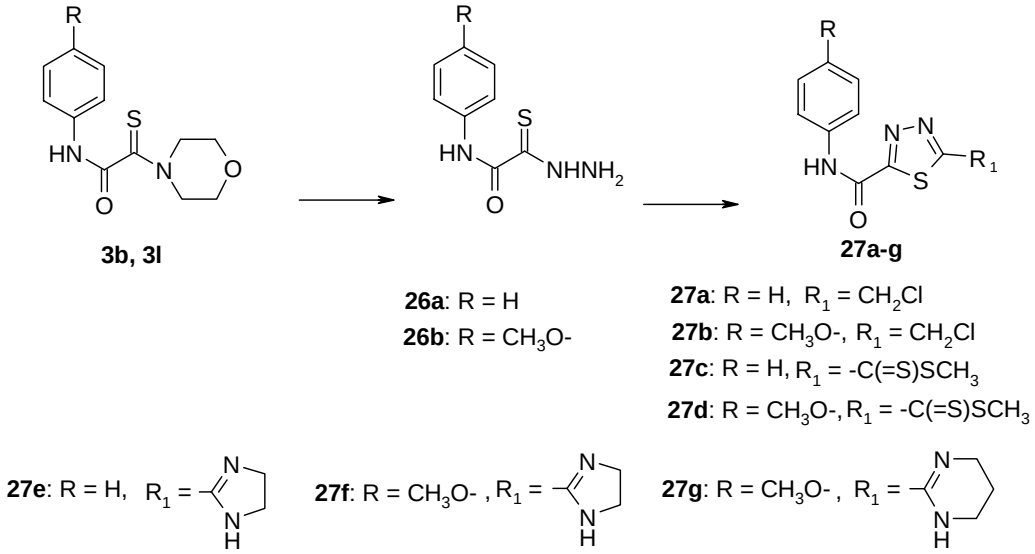
It should be noted that the reaction with O-methylhydroxylamine, which most likely possesses reducing properties (to a lesser extent than in hydroxylamine), [10] occurs less unambiguously than is the case with hydroxylamine, and depends on the substituents in the phenyl ring. Electron-donating substituents decrease the probability of reduction of the N-methoxy group to an amino group, and in the absence of substituents in the benzene ring, this group is hydrolyzed to some extent to form the hydroxamic acid **21**. It is noteworthy that the dimethoxyamide group (in compound **19**) has not been described previously.



Scheme 14

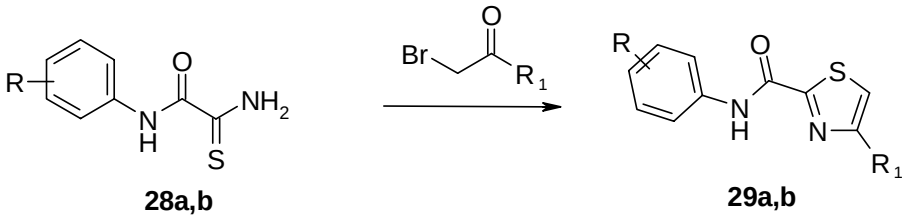
The monothio-oxamides have been used in syntheses of heterocyclic compounds. For example, iso-thioamides, prepared by the reaction of monothio-oxamides with dimethyl sulfate were used in a reaction with phenylthiosemicarbazide to afford the novel 2-carbamoyl-5-phenyl-1,3,4-thiadiazoles.

A wide range of thiadiazoles can be prepared by the heterocyclization of oxamic thiohydrazides followed by their chemical modification.



Scheme 15

The reactions of monothio-oxamides with α -haloketones afford the corresponding thiazoles.



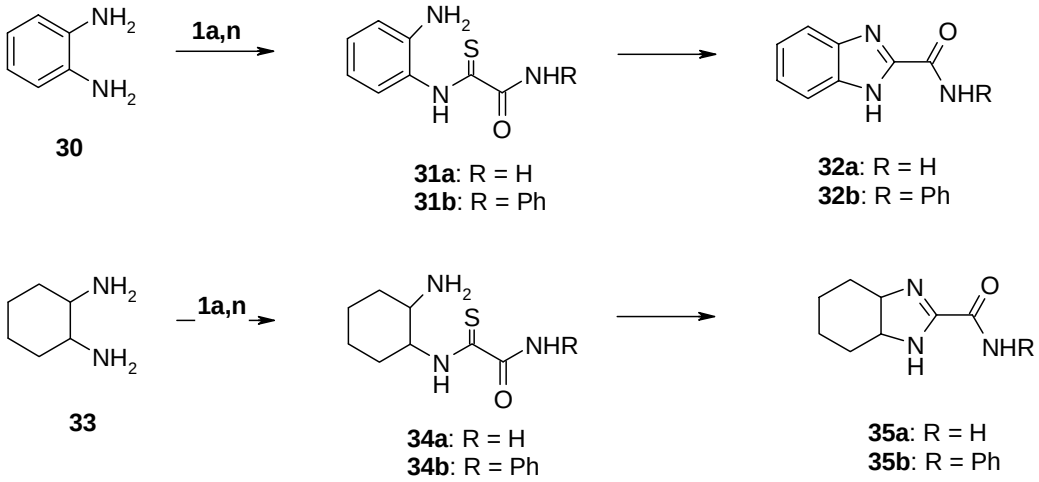
28a,b **29a,b**

28a: R = H
28b: R = 4-NO_2

29a: R = H, R_1 = 4-$(CH_3)C_6H_4$
29b: R = 4-NO_2, R_1 = 4-$(Br)C_6H_4$

Scheme 16

The reactions of aromatic and cyclic vicinal diamines with chloroacetamides form the monothio-oxamide at one of the amino groups, followed by a rapid heterocyclization involving the second amino group.

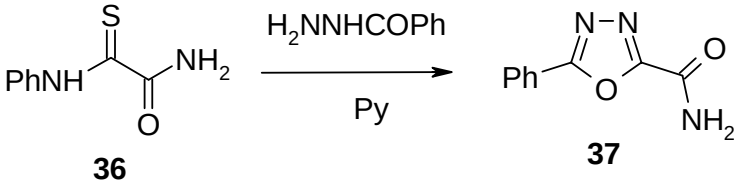


30 **31a**: R = H
31b: R = Ph
32a: R = H
32b: R = Ph

33 **34a**: R = H
34b: R = Ph
35a: R = H
35b: R = Ph

Scheme 17

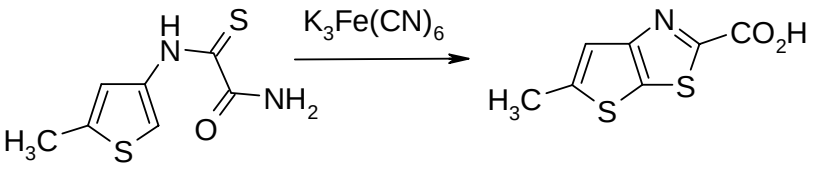
It is shown that the reaction of monothio-oxamide **36** with an acid hydrazide affords the 1,3,4-oxadiazole **37**.



36 **37**

Scheme 18

The intramolecular ring closure of a monothio-oxamide of the thiophene series occurs at 20°C under the action of $K_3Fe(CN)_6$ and is accompanied by hydrolysis of the amide group to form 2-carboxythieno[3,2-*d*]thiazole.



38 **39**

Scheme 19

Conclusions

Our study shows that monothio-oxamides are convenient starting compounds in the syntheses of a variety of oxamic acid derivatives and various mono- and di-heterocyclic compounds.

Experimental Section

General Procedures. The ^{1}H NMR spectra were measured on Bruker WM-250 instrument (250 MHz) in DMSO-d_6. Mass spectra (EI) were obtained on Kratos MS-30 instrument with a direct inlet of the sample into the ion source: the ionizing voltage was 70 eV, and the emission current, 0.1 mA. Melting points were determined on a Boetius stage and were not corrected. Column chromatography used silica gel (Merck 60, 70–230 mesh). Commercial reagents were purchased from Aldrich. RT denotes room temperature.

Synthesis of monothio-oxamides 3a,b according to a reported procedure.[6] Chloroacetamide **1a** (5.3 mmol), sulfur (0.7 g), and the amine (10 ml) were mixed and heated under reflux. The mixture was partitioned between ethyl acetate and water, and the organic phase washed with water, dried and evaporated. The reaction gave 3a (28%), mp 58–60°C (lit.[7] 58–60°C) and **3b** (57%), mp 164–166°C (lit.[6] 166°C). Neither the monothio-oxamide **18d**, nor **18e** was obtained by this procedure.

Synthesis of monothio-oxamide (3c). Compound **1b** was heated at reflux in DMF (10 mL) for 5 h. The reaction mixture was then diluted with water, and the precipitate filtered off. Crystallization from ethanol gave **3c** in (0.2 g, 62%), mp 142–143°C (EtOH). Anal. Calcd. for $C_{10}H_{12}N_2OS$: C, 57.69; H, 5.77; N, 13.46. Found: C, 57.73; H, 5.64; N, 13.57. ^{1}H NMR: 3.75 (6 H, s, CH_3), 7.10 (1 H, m, arom.), 7.30 (2 H, m, arom.), 7.70 (2 H, m, arom.), 9.65 (1H, s, NH).

Synthesis of monothio-oxamides (General Procedure A)

Chloroacetamide **1** (5 mmol) was added to a mixture of the appropriate amine (5.5 mmol) and sulfur (0.7 g) in 5 ml DMF. The reaction mixture was stirred at ca. 20°C for 8 h and diluted with

water. The precipitate that formed was filtered off, washed with water, and dried. The resulting product was dissolved in acetone (10 ml), the solution filtered, the acetone removed and the residue crystallized from 95% EtOH. The reaction gave **3a** (88%), mp 58–60°C (lit.[7] 58–60°C) and **3b** (92%), mp 165–166°C (lit.[6] 166°C).

Prepared similarly were:

3d. Yield 53%, mp 166–168°C. Anal. Calcd. for $C_{16}H_{15}ClN_4O_3S$: C, 50.73; H, 3.99; Cl, 9.36; N, 14.79. Found: C, 50.77; H, 9.89; Cl, 9.27; N, 14.86%. ^{1}H NMR: 3.65 (2 H, m, CH_2), 3.90 (2 H, m, CH_2), 3.90 (2 H, m, CH_2), 7.00 (2 H, m, arom.), 7.15 (1 H, t, *J* = 7.33 Hz, arom.), 7.40 (2 H, m, arom.), 7.65 (2 H, m, arom.), 8.05 (1 H, m, NH), 8.10 (1 H, s, arom.), 10.35 (1 H, s, NH), 11.10 (1 H, s, NH).

3e. Yield 86%, mp 100–101°C. Anal. Calcd. for $C_{14}H_{14}F_6N_2OS$: C, 45.16; H, 3.76; F, 30.64; N, 7.53. Found: C, 45.29; H, 3.63; F, 30.56; 7.62%. ^{1}H NMR: 1.25 (6 H, m, CH_3), 3.55 (2 H, m, CH_2), 3.95 (2 H, m, CH_2), 7.80 (1 H, m, arom.), 8.30 (2 H, m, arom.), 11.15 (1 H, s, NH).

3f. Yield 78%, mp 165–167°C (lit.[11] 165–167°C).

3g. Yield 73%, mp 186–187°C (lit. [11] 185–187°C).

3h. Yield 68%, mp 157–159°C. Anal. Calcd. for $C_{11}H_{12}ClN_3O_2S$: C, 46.24; H, 4.23; Cl, 12.41; N, 14.70. Found: C, 46.20; H, 4.30; Cl, 12.36; N, 14.61%. ^{1}H NMR: 3.78 (6 H, m, morphol.), 4.15 (2 H, m, morphol.), 7.50 (1 H, m, Py), 8.15 (1 H, d, *J* = 7.83 Hz Py), 8.30 (1 H, m, Py), 11.50 (1 H, s, NH).

3i. Yield 65%, mp 217–219°C. Anal. Calcd. for $C_{14}H_{15}N_2O_2S_2$: C, 61.09; H, 5.45; N, 10.18. Found: C, 61.17; H, 5.32; N, 10.22%. ^{1}H NMR: 2.35 (2 H, m, CH_2), 2.75 (2 H, m, CH_2), 2.85 (2 H, m, CH_2), 3.60 (2 H, m, morphol.), 3.70 (2 H, m, morphol.), 3.80 (2 H, m, morphol.), 4.15 (2 H, m, morphol.), 12.25 (1 H, s, NH).

5b. Yield 72%, mp 229–231°C. Anal. Calcd. for $C_{18}H_{22}N_4O_4S_2$: C, 51.17; H, 5.25; N, 13.26. Found: C, 51.04; H, 5.41; N, 13.29%. ^{1}H NMR: 7.35 (4 H, m, arom.), 7.45 (4 H, m, arom.), 7.75 (2 H, m, arom.), 7.95 (4 H, m, arom.), 10.60 (2 H, s, NH), 12.30 (2 H, s, NH).

18a. Yield 56%, mp 294–297°C. Anal. Calcd. for $C_{24}H_{28}N_4O_2S_2$: C, 61.51; H, 6.02; N, 11.96. Found: C, 61.58; H, 6.09; N, 12.05%. ^{1}H NMR: 2.25 (6 H, s, CH_3), 2.30 (6 H, s, CH_3), 4.05–4.18 (4 H, m, CH_2), 4.20–4.38 (4 H, m, CH_2), 7.10 (6 H, m, arom.), 10.00 (2 H, s, NH).

18b. Yield 64%, mp 135–139°C. Anal. Calcd. for $C_{18}H_{22}N_2OS$: C, 68.75; H, 7.05; N, 8.91. Found: C, 68.83; H, 6.95; N, 8.85%. ^{1}H NMR: 1.51–1.75 (7 H, m, Ad), 2.15 (3 H, m, Ad), 2.35 (5 H, m, Ad), 7.15 (1 H, t, *J* = 7.47 Hz, arom.), 7.38 (2 H, d, *J* = 7.68 Hz), 7.72 (2 H, d, *J* = 7.90 Hz, arom.), 9.78 (1 H, s, NH), 10.38 (1 H, s, NH).

18d. Yield 48%, mp 93–95°C (lit.[11] 93–95°C).

18e. Yield 67%, mp 85–86°C (lit.[11] 84–86°C).

18h. Yield 82%, mp 174–176°C. Anal. Calcd. for $C_{17}H_{16}Br_2N_2OS$: C, 44.76; H, 3.54; Br, 35.03; N, 6.14. Found: C, 44.69; H, 3.67; Br, 35.12; N, 6.07. ^{1}H NMR: 2.35 (3 H, s, CH_3), 3.00 (2 H, m, CH_2), 3.85 (2 H, m, CH_2), 7.20–7.40 (5 H, m, arom.), 10.25 (1 H, s, NH), 10.90 (1 H, s, NH).

Synthesis of monothio-oxamides (General Procedure B)

Chloroacetamide **1** (5 mmol) was added to a mixture of the aromatic amine (5.5 mmol), sulfur (0.7 g) and Et_3N (1 mL) in 5 ml DMF. The mixture was stirred at ca. 20 °C for 8 h and diluted

with water. The precipitate that formed was filtered off, washed with water and dried. The resulting compound was dissolved in acetone (10 mL), filtered, the acetone removed, and the residue crystallized from 95% EtOH.

5a. Yield 61%, mp 225–227°C. Anal. Calcd. for $C_{22}H_{18}N_4O_2S_2$: C, 60.81; H, 4.18; N, 12.89. Found: C, 60.87; H, 4.07; N, 12.93%. ^{1}H NMR: 3.65–3.85 (12 H, m, morphol.), 4.15 (4 H, m, morphol.), 7.30 (2 H, m, arom.), 7.65 (2 H, m, arom.), 9.95 (2 H, s, NH).

6a. Yield 58%, mp 166–167°C. Anal. Calcd. for $C_{16}H_{14}N_2O_3S$: C, 61.13; H, 4.49; N, 8.91. Found: C, 61.42; H, 4.66; N, 9.03%. ^{1}H NMR: 3.90 (3 H, s, CH_3), 7.20 (1 H, m, arom.), 7.40 (2 H, m, arom.), 7.80 (2 H, m, arom.), 8.05 (2 H, m, arom.), 10.50 (2 H, s, NH), 12.50 (1 H, s, NH).

6b. Yield 68%, mp 205–208°C. Anal. Calcd. for $C_{16}H_{15}N_3O_2S$: C, 61.32; H, 4.82; N, 13.41. Found: C, 61.42; H, 4.66; N, 14.01%. ^{1}H NMR: 2.10 (3 H, s, CH_3), 7.20 (1 H, m, arom.), 7.40 (2 H, d, J = 7.11 Hz, arom.), 7.65 (2 H, d, arom., J = 7.96 Hz), 7.80 (2 H, d, arom., J = 7.04 Hz), 7.95 (2 H, d, arom., J = 7.58 Hz), 10.00 (1 H, s, NH), 10.45 (1 H, s, NH), 12.50 (1 H, s, NH).

6c. Yield 53%, mp 108–109°C. Anal. Calcd. for $C_{18}H_{21}N_3OS$: C, 66.03; H, 6.46; N, 12.83. Found: C, 66.36; H, 6.14; N, 12.96%. ^{1}H NMR: 1.15 (6 H, m, CH_3), 3.55 (4 H, m, CH_2), 6.80 (2 H, m, arom.), 7.20 (1 H, m, arom.), 7.45 (2 H, m, arom.), 7.80 (2 H, m, arom.), 7.95 (2 H, m, arom.), 10.50 (1 H, s, NH), 12.05 (1 H, s, arom.).

6d. Yield 62%, mp 174–175°C. Anal. Calcd. for $C_{16}H_{13}N_3O_2S$. C, 61.72; H 4.21; N, 13.50. Found: C, 61.51; H, 4.27; N, 13.12%. ^{1}H NMR: 3.85 (3 H, s, CH_3), 7.05 (2 H, d, J = 8.91 Hz, arom.), 7.45 (1 H, t, J = 7.72 Hz, arom.), 7.80 (1 H, t, J = 7.74 Hz, arom.), 7.92 (3 H, m, arom.), 8.10 (1 H, d, J = 8.30 Hz, arom.), 10.90 (1 H, s, NH), 12.33 (1 H, s, NH).

6e. Yield 73%, mp 155–158°C. Anal. Calcd. for $C_{14}H_{10}C_{12}N_2OS$: C, 51.71; H, 3.10; C1, 21.80; N, 8.61. Found: C, 51.98; H, 3.03; C1, 21.63; N, 9.02%. ^{1}H NMR: 7.45 (2 H, d, J = 8.78 Hz, arom.), 7.55 (2 H, d, J = 8.76 Hz, arom.), 7.85 (2 H, d, J = 8.80 Hz, arom.), 8.00 (2 H, d, J = 8.78 Hz, arom.), 10.60 (1 H, s, NH), 12.40 (1 H, s, NH).

6f. Yield 57%, mp 171–174°C. Anal. Calcd. for $C_{16}H_{14}N_2O_3S$: C, 61.13; H, 4.49; N, 8.91. Found: C, 61.42; H, 4.66; N, 9.03%. ^{1}H NMR: 3.85 (3 H, s, CH_3), 7.35 (1 H, t, J = 8.12 Hz, arom.), 7.95 (2 H, m, arom.), 8.00 (6 H, m, arom.), 10.80 (1 H, s, NH), 12.40 (1 H, s, NH).

6g. Yield 67%, mp 198–200°C. Anal. Calcd. for $C_{12}H_{10}N_2OS$: C, 62.59; H, 4.38; N, 12.16. Found: C, 62.78; H, 4.16; N, 12.38. ^{1}H NMR: 7.55 (4 H, m, arom.), 7.72 (1 H, m, arom.), 8.00 (2 H, m, arom.), 8.15 (2 H, m, NH_2), 12.35 (1 H, s, NH).

7a. Yield 77%, mp 160–162°C. Anal. Calcd. for $C_7H_7N_3OS$: C, 46.40; H, 3.89; N, 23.19. Found: C, 46.66; H, 3.76; N, 23.23%. ^{1}H NMR: 7.40 (1 H, m, Py), 8.00 (1 H, t, Py, J = 7.70 Hz), 8.25 (2 H, s, NH_2), 8.55 (1 H, m, Py), 8.82 (1 H, d, J = 8.21 Hz, Py), 11.80 (1 H, s, NH).

7b. Yield 67%, mp 195–198°C. Anal. Calcd. for $C_7H_6BrN_3OS$: C, 32.32; H, 2.33; Br, 30.72; N, 16.15. Found: C, 32.28; H, 2.36; Br, 30.84; N, 16.07%. ^{1}H NMR: 8.20 (3 H, m, Py), 8.65 (2 H, m, NH_2), 11.95 (1 H, s, NH).

7c. Yield 35%, mp 210–212°C. Anal. Calcd. for $C_7H_7N_3OS$: C, 46.40; H, 3.89; N, 23.19. Found: C, 46.37; H, 3.92; N, 23.23%. ^{1}H NMR: 8.12 (4 H, m, Py), 8.65 (2 H, m, NH_2), 12.25 (1 H, s, NH).

7d. Yield 58%, mp 218–224°C. Anal. Calcd. for $C_{11}H_{13}N_3O_2S_2$: C, 46.62; H, 4.62; N, 14.83. Found: C, 46.76; H, 4.06; N, 14.86. ^{1}H NMR: 2.80 (4 H, m, -CH_2CH_2-), 2.65–2.90 (4 H, m CH_2), 7.50 (2 H, s, NH_2), 8.10 (2 H, m, NH_2), 14.5 (1 H, s, NH).

9. Yield 69%, mp 239–241°C. Anal. Calcd. for $C_9H_8N_4OS$: C, 49.08; H, 3.66; N, 25.44. Found: C, 50.06; H, 3.29; N, 25.12%. ^{1}H NMR: 6.12 (2 H, s, NH_2), 6.92 (2 H, d, arom., J = 9.11 Hz), 7.92 (2 H, d, J = 9.20 Hz, arom.), 8.00–8.10 (2 H, m, NH_2), 8.13 (1 H, s, arom.), 11.95 (1 H, s, NH).

11. Yield 71%, mp 130–133°C. Anal. Calcd. for $C_9H_{11}N_3OS$: C, 51.66; H, 5.03; N, 20.08. Found: C, 51.87; H, 4.96; N, 20.13%. ^{1}H NMR: 2.62 (3 H, s, CH_3), 5.95 (1 H, s, NH), 6.55 (2 H, d, J = 9.05 Hz), arom., 7.85 (2 H, d, J = 8.92 Hz, arom.), 8.0–8.15 (2 H, m, NH_2), 1175 (1 H, s, NH).

13. Yield 70%, mp 209–212°C. Anal. Calcd. for $C_{14}H_{13}N_3O_3S_2$: C, 50.14; H, 3.93; N, 12.53. Found: C, 50.36; H, 4.01; 12.27%. ^{1}H NMR: 6.12 (2 H, s, NH_2), 6.65 (2 H, d, arom., J = 8.64 Hz), 7.55 (2 H, d, J = 8.55 Hz, arom.), 7.90 (2 H, d, J = 8.61 Hz, arom.), 8.12 (2 H, m, NH_2), 8.18 (2 H, d, J = 8.50 Hz, arom.), 12.25 (1 H, s, NH).

15. Yield 53%, mp 228–230°C. Anal. Calcd. for $C_{20}H_{15}N_5O_2S$: C, 61.70; H, 6.25; N, 17.99. Found: C, 61.86; H, 6.12; N, 18.06%. ^{1}H NMR: 6.00 (2 H, s, NH_2), 6.70 (2 H, m, arom.), 7.30 (1 H, m, arom.), 7.80 (2 H, m, arom.), 7.90 (2 H, m, arom.), 7.95 (1 H, m, Py), 8.20 (1 H, m, Py), 8.30 (1 H, m, Py), 8.45 (1 H, m, Py), 10.65 (1 H, s, NH), 12.60 (1 H, s, NH).

17a. Yield 58%, mp 270–271°C. Anal. Calcd. for $C_9H_{11}N_3O_2S_2$: C, 42.02; H, 4.28; N, 16.34. Found: C, 41.96; H, 4.35; N, 16.28%. ^{1}H NMR: 3.65 (2 H, m, morphol.), 3.70 (2 H, m, morphol.), 3.80 (2 H, m, morphol.), 4.15 (2 H, m, morphol.), 7.45 (1 H, d, J = 3.62 Hz, thiazole), 7.65 (1 H, d, J = 3.49 Hz, thiazole), 12.70 (1 H, s, NH).

17b. Yield 62%, mp 197–200°C. Anal. Calcd. for $C_{10}H_{14}N_4OS_2$: C, 44.42; H, 5.22; N, 20.70. Found: C, 44.62; H, 5.13; N, 20.63%. ^{1}H NMR: 2.28 (3 H, s, CH_3), 2.55 (4 H, m, morphol.), 3.60 (2 H, m, morphol.), 4.12 (2 H, m, morphol.), 7.30 (1 H, d, J = 3.37 Hz, thiazole), 7.55 (1 H, d, J = 3.41 Hz, thiazole), 12.55 (1 H, s, NH).

17c. Yield 56%, mp 181–183°C. Anal. Calcd. for $C_{11}H_8BrN_3OS_2$: C, 38.61; H, 2.36; Br, 23.35; N, 12.28. Found: C, 38.45; H, 2.48; Br, 23.57; N, 12.04%. ^{1}H NMR: 7.40 (1 H, d, J = 3.61 Hz, thiazole), 7.60 (1 H, d, J = 3.53 Hz, thiazole), 7.65 (2 H, d, J = 8.74 Hz, arom.), 7.95 (2 H, d, J = 8.72 Hz, arom.), 12.30 (1 H, s, NH), 12.55 (1 H, s, NH).

18c. Yield 76%, mp 188–190°C. Anal. Calcd. for $C_8H_7BrN_2OS$: C, 37.08; H, 2.72; Br 30.84; N, 10.81. Found: C, 37.02; H, 2.97; Br, 30.90; N, 10.73%. ^{1}H NMR: 7.30 (1 H, t, J = 7.78 Hz, arom.), 7.45 (1 H, t, J = 7.65 Hz, arom.), 7.75 (2 H, m, arom.), 8.15 (2 H, m, NH_2), 12.00 (1 H, s, NH_2).

18f. Yield 42%, mp 92–94°C. Anal. Calcd. for $C_{17}H_{14}N_2O_2S$: C, 65.79; H, 4.55; N, 9.03. Found: C, 65.82; H, 4.50; N, 9.44%. ^{1}H NMR: 3.20 (1 H, m, CH), 3.75 (1 H, m, CH), 7.25–7.75 (10 H, m, arom.), 8.05 (2 H, m, NH_2).

18g. Yield 64%, mp 190–192°C. Anal. Calcd. for $C_{16}H_{15}N_3O_3S$: C, 58.35; H, 4.59; N, 12.67. Found: C, 58.39; H, 4.56; N, 12.78%. ^{1}H NMR: 2.20 (6 H, s, CH_3), 7.20 (3 H, m, arom.), 8.15 (2

H, d, *J* = 9.23 Hz, arom.), 8.35 (2 H, d, *J* = 9.23 Hz, arom.), 11.00 (1 H, s, NH), 12.22 (1 H, s, NH).

38. The starting 2-methyl-4-aminothiophene was prepared according to a reported procedure.[12] Yield 60%, mp 148–150°C (EtOH). Anal. Calcd. for $C_7H_8N_2OS_2$: C, 42.00; H, 4.00; N, 14.00. Found: C, 42.03; H, 4.05; N, 13.92%. ^{1}H NMR: 2.50 (3 H, s, CH_3), 5.78 (1 H, s, NH_2), 6.95 (1 H, s, thiophene), 8.10 (1 H, s, NH_2), 8.45 (1 H, s, thiophene), 11.25 (1 H, s, NH). Mass spectrum: *m*/*z* 200 [M].

Synthesis of O-methyl-oximes 19 and 20

O-Methylhydroxylamine (5 mmol) was added to a solution of the monothio-oxamide **3l** (or **3m**) (1 mmol) in pyridine (7 mL). The mixture was heated at reflux for 7 h, cooled, diluted with water, and extracted with ethyl acetate. The organic layer was washed with 2% HCl, dried, the solvent removed, and the residue purified by column chromatography using ethyl acetate–hexane (1:1) mixture as eluent.

19. Yield, 47.2%, mp 96–98°C (EtOH). Anal. Calcd. for $C_{11}H_{15}N_3O_4$: C, 52.17; H, 5.97; N, 16.59. Found: C, 52.21; H, 6.09; N, 16.45%. ^{1}H NMR: 3.60 (3 H, s, CH_3), 3.70 (3 H, s, CH_3), 3.80 (3 H, s, CH_3), 6.90 (2 H, d, *J* = 8.90 Hz, arom.), 7.60 (2 H, d, *J* = 8.91 Hz, arom.), 9.61 (1 H, s, NH), 10.28 (1 H, s, NH). Mass spectrum: *m*/*z* 253 [M].

20. Yield 27%, mp 125–128°C (EtOH). Anal. Calcd. for $C_{11}H_{15}N_3O_2$: C, 59.71; H, 6.83; N, 18.99. Found: C, 59.80; H, 6.87; N, 18.90%. ^{1}H NMR: 2.20 (3 H, s, CH_3), 2.28 (3 H, s, CH_3), 3.85 (3 H, s, CH_3), 6.02 (2 H, s, NH_2), 7.05 (2 H, m, arom.), 7.30 (2 H, d, *J* = 6.93 Hz, arom.), 9.30 (1 H, s, NH). Mass spectrum: *m*/*z* 221 [M].

Synthesis of the hydroxamic acid 21

O-Methylhydroxylamine (0.42 g, 5 mmol) was added to a solution of the monothio-oxamide **3b** (0.25 g, 1 mmol) in pyridine (7 mL). The mixture was heated at reflux for 7 h, cooled, and diluted with water. The precipitate was filtered off, washed with 2% HCl, and dried to give the product (0.15 g). This was purified by column chromatography using ethyl acetate–hexane (1:1) as eluent to give the product (0.1 g, 52%), m.p. 143–145°C (EtOH). Anal. Calcd. for $C_9H_{10}N_2O_3$: C, 55.69; H, 5.15; N, 14.43. Found: C, 55.43; H, 5.19; N, 14.61%. ^{1}H NMR: 3.10 (3 H, s, CH_3), 7.17 (1 H, m, arom.), 7.38 (2 H, m, arom.), 7.75 (d, arom., *J* = 7.93 Hz). Mass spectrum: *m*/*z* 194 [M].

Synthesis of 22a,b

A mixture of monothio-oxamide **3b** (0.8 mmol) and dimethyl sulfate (2.4 mmol) was heated for 45 min at 100°C followed by cooling to RT. The resulting mixture was dissolved in DMF (5 ml), the amine (2 mmol) was added, the mixture was stirred for 2 h, poured into water, and the precipitate filtered off and recrystallized from ethanol.

22a. Yield 30%, mp 143–146°C. Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64,83; H, 6.02; N, 13.53%. ^{1}H NMR: 3.80 (2 H, m, CH_2), 5.20 (2 H, m, CH_2), 5.80 (1

H, m, CH), 7.10 (1 H, t, *J* = 7.61 Hz, arom.), 7.30 (2 H, t, *J* = 7.61 Hz, arom.), 7.60 (2 H, d, *J* = 7.92 Hz, arom.), 11.40 (1 H, s, NH).

22b. Yield 43%, mp 171–174°C. Anal. Calcd. for $C_{16}H_{14}N_2O_3$: C, 68.08; H, 5.00; N, 9.92. Found: C, 68.14; H, 4.92; N, 9.83%. ^{1}H NMR: 4.70 (2 H, m, CH_2), 7.10 (1 H, t, *J* = 7.37 Hz, arom.), 7.30 (2 H, t, *J* = 7.61 Hz, arom.), 7.50 (1 H, t, *J* = 7.37 Hz, arom.), 9.10 (1 H, s, NH), 10.65 (1 H, s, NH).

Synthesis of 22c

A mixture of the monothio-oxamide **3j** (0.8 mmol) and silver nitrate (1.6 mmol) was boiled for 10 min in 50% aqueous acetonitrile (4 ml). Then the mixture was filtered through silica gel, washed with ethyl acetate, the solvent evaporated, and the residue recrystallized from ethanol. Yield 63%, mp 160–162°C (EtOH). Anal. Calcd. for $C_{12}H_{13}ClN_2O_3$: C, 53.64; H, 4.88; Cl, 13.22; N, 10.39. Found: C, 53.91; H, 478; Cl, 13.38; N, 10.43%. ^{1}H NMR: 3.20–3.60 (8 H, m, morph.), 7.40 (2 H, d, *J* = 8.73 Hz, arom.), 7.70 (2 H, d, *J* = 8.72 Hz, arom.), 10.80 (1 H, s, NH).

Synthesis of 23

A mixture of monothio-oxamide **3b** (0.2 g, 0.8 mmol) and dimethyl sulfate (0.4 ml, 0.3 g, 2.4 mmol) was heated for 45 min at 100°C followed by cooling to RT. Then H_2S was passed through the mixture for 7 h, and the mixture poured into water. The precipitate was filtered off and recrystallized from ethanol. Yield of **23** 32%, mp 78–80°C (lit.[12] 78–80°C).

Synthesis of oxalic thioesters 24a–c

A mixture of the monothio-oxamide **3b** (0.2 g, 0.8 mmol) and dimethyl sulfate (0.4 ml, 0.3 g, 2.4 mmol) was heated for 45 min at 100°C, and then water (10 ml) was added. The precipitate was filtered off and recrystallized from hexane.

24a. Yield 68%, mp 111–114°C. Anal. Calcd. for $C_9H_9NO_2S$: C, 55.37; H, 4.65; N, 7.17. Found: C, 55.41; H, 4.61; N, 7.14%. ^{1}H NMR: 2.40 (3 H, s, CH_3), 7.10 (2 H, d, *J* = 7.36 Hz, arom.), 7.30 (2 H, t, *J* = 7.61 Hz), 7.80 (2 H, d, *J* = 7.92 Hz, arom.), 10.65 (1 H, s, NH).

24b. Yield 74%, mp 165–168°C. Anal. Calcd. for $C_9H_8ClNO_2S$: C, 47.06; H, 3.51; N, 6.10. Found: C, 47.29; H, 3.42; N, 6.23%. ^{1}H NMR: 2.40 (3 H, s, CH_3), 7.41 (2 H, d, *J* = 8.73 Hz, arom.), 7.92 (2 H, d, *J* = 8.72 Hz, arom.), 10.80 (1 H, s, NH).

24c. Yield 72%, mp 254–258°C. Anal. Calcd. for $C_9H_{10}N_2O_4S_2$: C, 39.41; H, 3.41; N, 10.21. Found: C, 39.11; H, 3.62; N, 10.34%. ^{1}H NMR: 2.40 (3 H, s, CH_3), 7.20 (2 H, s, NH_2), 7.80 (2 H, d, *J* = 8.94 Hz, arom.), 8.00 (2 H, d, *J* = 8.77 Hz, arom.), 10.90 (1 H, s, NH).

Synthesis of 25a,b

A mixture of monothio-oxamide **3b** (or **3j**) (0.8 mmol) and dimethyl sulfate (2.4 mmol) was heated for 45 min at 100°C, then cooled to RT. The mixture was then dissolved in DMF (5 ml), the amine (2 mmol) was added, and the mixture stirred for 2 h, then poured into water, and the precipitate formed was filtered off and recrystallized from ethanol.

25a. Yield 59%, mp 254–255°C. Anal. Calcd. for $C_{15}H_{12}N_4OS$: C, 60.79; H, 4.08; N, 18.91. Found: C, 61.01; H, 4.12; N, 18.70%. ^{1}H NMR: 7.10 (2 H, m, arom.), 7.35 (4 H, m, arom.), 7.65 (2 H, m, arom.), 7.75 (2 H, m, arom.), 10.80 (1 H, s, NH).
25b. Yield 67%, mp >260°C. Anal. Calcd. for $C_{15}H_{11}C1N_4OS$: C, 54.46; H, 3.35; C1, 10.72; N, 16.94. Found: C, 54.75; H, 3.38; Cl, 11.01; N, 16,69%. ^{1}H NMR: 7.10 (1 H, m, arom.), 7.35 (4 H, m, arom.), 7.65 (2 H, m, arom.), 7.75 (2 H, m, arom.), 10.80 (1 H, s, NH).

Synthesis of 27c,d

A mixture of sulfur (1 mmol) and triethylamine (0.5 ml) in DMF (1 ml) was stirred for 30 min. Then a solution of **27a** (or **27b**)[13] (0.3 mmol) in DMF (1 ml) was added, the mixture stirred for 1.5 h at RT, and then MeI (4 mmol) was added. After 3 h, the mixture was poured into water, and the precipitate filtered off and dried. To remove unreacted sulfur, the product was dissolved in acetone, the solution separated, and the solvent evaporated *in vacuo*. The solid residue was recrystallized from acetonitrile.
27c. Yield 57%, mp 144–145°C. Anal. Calcd. for $C_{11}H_9N_3OS_3$: C, 44.73; H, 3.07; N, 14.22. Found: C, 44.62; H, 3.25; N, 14.03%. ^{1}H NMR: 2.80 (3 H, s, CH_3), 7.10 (1 H, t, J = 7.37 Hz, arom.), 7.30 (2 H, t, J = 7.61 Hz, arom.), 7.60 (2 H, d, J = 7.92 Hz, arom.), 11.40 (1 H, s, NH).
27d. Yield 52%, mp 150–153°C. Anal. Calcd. for $C_{12}H_{11}N_3O_2S_3$: C, 44.29; H, 3.41; N, 12.91. Found: C, 44.31; H, 3.38; N, 12.67%. ^{1}H NMR: 2.80 (3 H, s, CH_3), 6.90 (2 H, d, J = 8.83 Hz, arom.), 7.80 (2 H, d, J = 8.84 Hz, arom.), 11.20 (1 H, s, NH).

Syntheses of 27e–g

The appropriate diamine (0.3 mmol) was added to a solution of the thio-ester (0.1 mmol) in DMF (2 ml), and the mixture left overnight. Then the mixture was poured into water (20 ml), and the precipitate filtered off and recrystallized from acetonitrile.
27e. Yield 62%, mp 262–265°C. Anal. Calcd. for $C_{12}H_{11}N_5OS$: C, 52.73; H, 4.06; N, 25.62. Found: C, 52.67; H, 3.99; N, 25.47%. ^{1}H NMR: 3.40 (4 H, m, -CH_2CH_2-), 7.10 (1 H, t, J = 7.73 Hz, arom.), 7.30 (2 H, t, J = 7.61 Hz, arom.), 7.80 (2 H, d, J = 7.92 Hz, arom.), 10.65 (1 H, s, NH).
27f. Yield 54%, mp 264–268°C. Anal. Calcd. for $C_{13}H_{13}N_5O_2S$: C, 51.47; H, 4.32; N, 23.09. Found: C, 51,54; H, 4.25; N, 23.01%. ^{1}H NMR: 3.40 (4 H, m, -CH_2CH_2-), 3.70 (3 H, s, CH_3), 6.90 (2 H, d, J = 8.83 Hz, arom.), 7.80 (2 H, d, J = 8.84 Hz, arom.), 11.20 (1 H, s, NH).
27g. Yield 41%, mp 204–206°C. Anal. Calcd. for $C_{14}H_{15}N_5O_2S$: C, 53.02; H, 4.76; N, 22.07. Found: C, 53.02; H, 4.67; N, 22.13%. ^{1}H NMR: 1.80 (2 H, m, CH_2), 3.40 (4 H, m, CH_2), 3.70 (3 H, s, CH_3), 6.90 (2 H, d, J = 8.83 Hz, arom.), 7.80 (2 H, d, J = 8.84 Hz, arom.), 11.20 (1 H, s, NH).

Synthesis of thiazolecarboxamides 29a,b

A solution of the monothio-oxamide **28a** (or **28b**) (2 mmol) and bromoacetophenone (2 mmol) in acetic acid (10 mL) was heated at reflux for 48 h. The acetic acid was removed *in vacuo*, and aqueous ammonia was added to the residue. The precipitate that formed was filtered off, and the

desired thiazolecarboxamide isolated by column chromatography (silica gel, ethyl acetate–hexane, 1:1 as eluent).

29a. Yield 73%, mp 119–121°C. Anal. Calcd. for $C_{17}H_{14}N_2OS$: C, 69.36; H, 4.79; N, 9.52. Found: C, 69.38; H, 4.77; N, 9.51%. ^{1}H NMR: 2.37 (3 H, s, CH_3), 7.17 (1 H, t, *J* = 7.35 Hz, arom.), 7.32 (2 H, d, *J* = 7.89 Hz, arom.), 7.40 (2 H, t, *J* = 7.53 Hz, arom.), 7.86 (2 H, d, *J* = 7.96 Hz, arom.), 8.05 (2 H, d, *J* = 7.96 Hz, arom.), 8.38 (1 H, s, thiazole), 10.51 (1 H, s, NH).

29b. Yield 75%, mp 227–229°C. Anal. Calcd. for $C_{16}H_{10}BrN_3O_3S$: C, 47.54; H, 2.49; N, 10.39. Found: C, 47.57; H, 2.58; N, 10.26%. ^{1}H NMR: 7.72 (2 H, d, *J* = 8.04 Hz, arom.), 8.14 (4 H, m, arom.), 8.30 (2 H, m, arom.), 8.60 (1 H, s, thiazole), 11.12 (1 H, s, NH).

Synthesis of 32a,b and 35a,b

Chloroacetamide **1** (5 mmol) was added to a prepared mixture of the aromatic amine (5.5 mmol), sulfur (0.7 g) and Et_3N (1 mL) in 5 ml DMF. The reaction mixture was stirred at 40–50°C for 8 h, diluted with water, and extracted with ethyl acetate. The organic layer was washed with water and dried. After removal of solvent, the residue was purified by column chromatography using ethyl acetate–hexane (1:1) as eluent.

32a. Yield 42%, mp ~300°C (lit.[14] >300°C). Mass spectrum: *m*/*z* 161 [M].

32b. Yield 35%, mp 233–235°C (lit.[15] 234–235°C).

35a. Yield 56%, mp 208–210°C. Anal. Calcd. for $C_8H_{13}N_3O$: C, 57.47; H, 7.84; N, 25.13. Found: C, 57.53; H, 7.89; N, 25.46%. ^{1}H NMR: 1.25–1.75 (8 H, m, -$(CH_2)_4$-), 3.80 (2 H, m, CH), 7.65–7.75 (2 H, m, NH_2).

35b. Yield 53%, mp 185–186°C. Anal. Calcd. for $C_{14}H_{17}N_3O$: C, 69.11; H, 7.04; N, 17.27. Found: C, 69.27; H, 6.94; N, 17.36%. ^{1}H NMR: 1.25–1.85 (8 H, m, -$(CH_2)_4$-), 3.80 (2 H, t, *J* = 11.53 Hz, CH), 7.12 (1 H, t, *J* = 7.18 Hz, arom.), 7.35 (2 H, m, arom.), 7.80 (2 H, d., *J* = 8.26 Hz, arom), 10.30 (1 H, s, NH).

Synthesis of 37

A solution of monothio-oxamide **36** (2 mmol) and benzoic acid hydrazide (2 mmol) in pyridine (10 mL) was heated at reflux for 48 h. The mixture was cooled, diluted with water, extracted with ethyl acetate, and the organic layer washed with 2% HCl and dried. The residue after removal of solvent was purified by column chromatography using ethyl acetate–hexane (1:1) as eluent. Yield of **37** 18%, mp 174–175°C (lit.[17] 174.5–176°C).

Synthesis of 39

Compound **38** (0.3 g, 0.0015 mmol) was dissolved in a 20% NaOH solution (60 ml), and $K_3Fe(CN)_6$ (1.08 g, 0.0033 mol) in water (5 ml) added with stirring. The mixture was stirred for 72 h at RT, then acidified (aq. HCl) to pH 5, and the precipitate filtered off and dried. The reaction gave **39**, mp 95–97°C in 40% yield. Anal. Calcd. for $C_7H_5NO_2S_2$: C, 42.21; H, 2.51; N, 32.16. Found: C, 42.20; H, 2,55; N, 7.03%. ^{1}H NMR: 2.56 (3 H, s, CH_3), 4.12 (1 H, s, OH), 7.35 (1 H, s, thiophene). Mass spectrum: *m*/*z* 199 [M].

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