Synthesis of monothiooxamides

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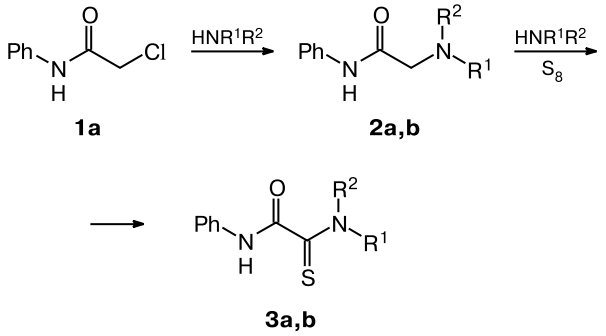
A convenient method for the synthesis of monothiooxamides by the reaction of chloroacetamides with a solution of elemental sulfur in amines was developed.

Key words: chloroacetamides, sulfur, amines, monothiooxamides.

Monothiooxamide fragments are present in natural products.[1] Currently, monothiooxamides are under intensive research as biologically active compounds.[2,3] Of particular interest is the use of monothiooxamides as complexing structures.[4] However, despite the high synthetic potential, these compounds have been little studied before the beginning of our works,[5] mainly due to the lack of convenient methods for their synthesis.

In our opinion, most promising is the synthesis of monothiooxamides based on the reaction of chloroacetamides with elemental sulfur and amines. Several examples of this reaction have been described in the literature.[6,7] However, this approach has a number of substantial drawbacks, including the necessity of long-term heating of the reaction mixture. It is known[8] that on heating, sulfur reacts with amines to give a mixture of products and this can complicate the synthesis of monothiooxamides. Previously,[7] we showed that simultaneous addition of elemental sulfur and amine to chloroacetamide **1a** gives a substantial amount of α-aminoacetamides **2a,b**, which then react with sulfur to give monothiooxamides **3a,b** only on long-term heating (Scheme 1).

Scheme 1

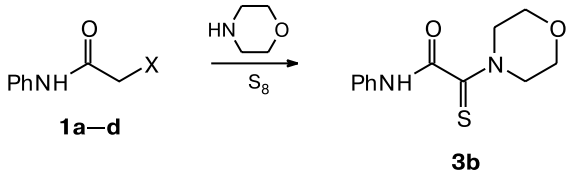


1a **2a,b** **3a,b**

R^1 = H, R^2 = Bu^n (**a**); R^1R^2 = —$(CH_2)_2$—O—$(CH_2)_2$— (**b**)

In this study, we showed that monothiooxamides can be obtained in high yields under mild conditions by using a specially prepared solution of sulfur in the required amine (stirring of the components for 20—30 min). The effects of the solvent, the nature of the substituent located in the α-position of the amide, and the substituents in the "acetamide" and "amine" components were studied. It was found that S-functionalization of chloroacetamides proceeds most smoothly, the yield of monothiooxamide **3b** being 92%. In other cases, the product yield did not exceed 25% (Scheme 2).

Scheme 2

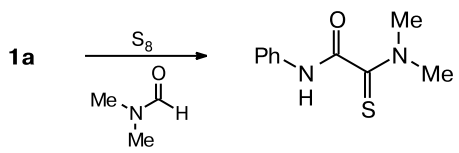


1a—d **3b**

X = Cl (**a**), SPh (**b**), $SCONH_2$ (**c**), $S_2CH_2CONHPh$ (**d**)

The solvents of choice for this reaction are dimethylformamide and an excess of the amine. We found that only the mild reaction conditions (≈20 °C) enable the use of DMF, because on heating, it reacts with chloroacetamide **1a** and sulfur to give the corresponding monothiooxamide **3c**, which contains a dimethylamino group in the thioamide fragment (Scheme 3).

Scheme 3



3c

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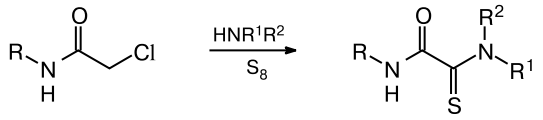
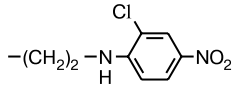
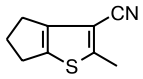
The nature of the substituent located in the acetamide fragment does not affect significantly the sulfurization of chloroacetamides. Compounds containing electron-withdrawing or electron-releasing substituents react almost identically with a solution of elemental sulfur in an amine. The synthesis of monothiooxamides **3d—i** is shown in Scheme 4.

Scheme 4

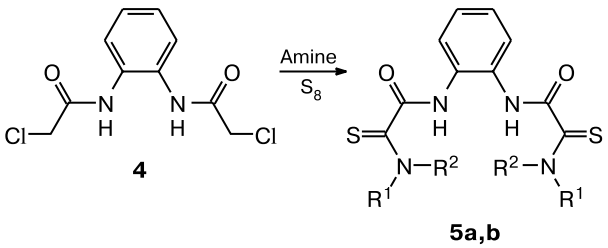


1a, f—j **3d—i**

Compound	R	**3**	R^1	R^2
1a, **3d**	Ph	**d**	H	
1f, **3e**	3,5-$(CF_3)_2C_6H_3$	**e**	Et	Et
1g, **3f**	3-$(NO_2)C_6H_4$	**f**		$-(CH_2)_5-$
1h, **3g**	3,4-$Cl_2C_6H_3$	**g**		$-(CH_2)_5-$
1i, **3h**		**h**	$-(CH_2)_2-O-(CH_2)_2-$	
1j, **3i**		**i**	$-(CH_2)_2-O-(CH_2)_2-$	

This method allows one to synthesize bis-monothiooxamides. Thus products **5a,b** were prepared from chloroacetamide **4** (Scheme 5).

Scheme 5

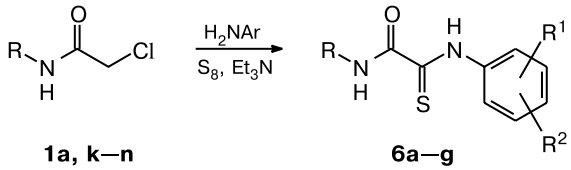


4 **5a,b**

R^1 = H, R^2 = Ph (**a**); $R^1R^2 = -(CH_2)_2-O-(CH_2)_2-$ (**b**)

The influence of substituents in the "amine" component proved to be more significant. In the reaction with anilines, which are weaker bases than aliphatic amines, triethylamine should be added to the reaction mixture as the catalyst. The reaction gives diverse monothiooxamides **6a—g** (Scheme 6).

Scheme 6

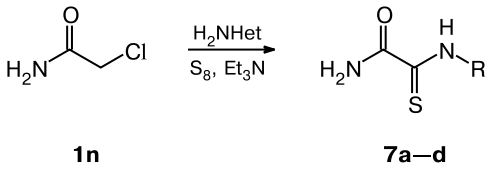


1a, k—n **6a—g**

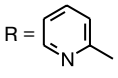
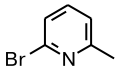
1	R	**6**	R	R^1	R^2
k	2-CNC_6H_4	**a**	Ph	H	4-MeOCO
l	4-$MeOCOC_6H_4$	**b**	Ph	H	4-MeCONH
m	4-ClC_6H_4	**c**	Ph	H	4-Et_2N
n	H	**d**	2-CNC_6H_4	H	4-MeO
		e	4-ClC_6H_4	H	4-Cl
		f	4-$MeOCOC_6H_4$	H	H
		g	H	2,3-CH=CH—CH=CH—	

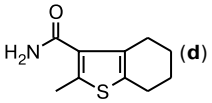
Heteroaromatic amines also form monothiooxamides when react with chloroacetamides in the presence of triethylamine. The synthesis of monothiooxamides **7a—d** is presented in Scheme 7.

Scheme 7



1n **7a—d**

R =  (**a**),  (**b**),  (**c**),

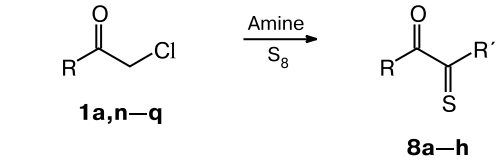
 (**d**)

The steric effects do not influence much the course of the reaction and this allows one to use sterically hindered chloroacetamides (**1o,p**) and amines (2,6-dimethylaniline, 2,6-dibromo-4-methylaniline, 2-bromoaniline, aminoadamantane). Owing to mild reaction conditions, relatively unstable amines such as cyclopropylamine, allylamine, or aziridines can also be introduced in the reaction (Scheme 8).

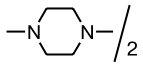
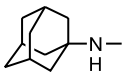
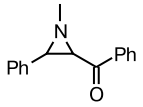
One more advantage of the method is the possibility of preparing monothiooxamide isomers. This is attained by changing the positions of the "amine" and "acetamide" reaction components (Scheme 9).

Thus, we demonstrated that the use of a preliminarily prepared solution of sulfur in amines is fairly convenient for S-functionalization of α-chloroacetamides, resulting in the formation monothiooxamides.

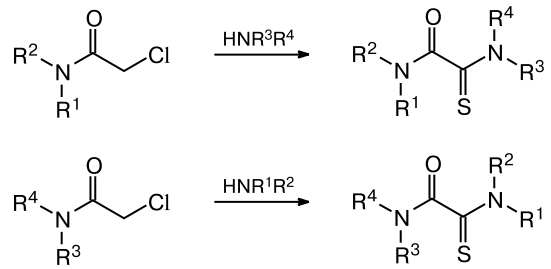
Scheme 8



Compound	R
1a, **8b,d,e**	PhNH—
1n, **8c,f**	NH_2
1o, **8a**	2,6-$Me_2C_6H_3NH$—
1p, **8h**	2,6-Br_2-4-MeC_6H_2NH—
1q, **8g**	4-$NO_2C_6H_4NH$—

8	R′	**8**	R′
a		**e**	CH_2=CH—CH_2—NH—
b		**f**	
c	2-BrC_6H_4NH—	**g**	2,6-$Me_2C_6H_3NH$—
d		**h**	$PhCH_2CH_2NH$—

Scheme 9



Experimental

^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250 MHz) in DMSO-d_6. Mass spectra were measured on a Kratos MS-30 instrument with direct sample injection into the ion source and with 70 eV ionizing radiation. Melting points were determined on a Boetius hot stage and were not corrected. Column chromatography was carried out on silica gel (Merck 60, 70—230 mesh). Commercial chemicals (Aldrich) were used. Chloroacetamides were synthesized by a known procedure.[9]

***N*(S)-Butyl-*N*(O)-phenylthiooxamide (3a) and 2-morpholino-2-thioxoacetanilide (3b)** were prepared by a previously described procedure.[6] Chloroacetamide **1a** (5.3 mmol), sulfur (0.7 g), and an amine (10 mL) were mixed and refluxed for 1 h. Then the mixture was cooled, diluted with water and extracted with AcOEt. The organic layer was washed with water and dried over $MgSO_4$. After removal of the solvent, the product was recrystallized from ethanol. The yield of thiooxamide **3a** was 28%, m.p. 58—60 °C (*cf.* Ref. 7: 58—60 °C). Under similar conditions, the yield of thiooxamide **3b** was 57%, m.p. 164—166 °C (*cf.* Ref. 6: 166 °C).

Synthesis of *N*(S),*N*(S)-dimethyl-*N*(O)-phenylthiooxamide (3c). Chloroacetamide **1a** (5.3 mmol) and sulfur (0.7 g) in 10 mL of DMF were refluxed for 5 h. The mixture was cooled and diluted with water and the precipitate was filtered off. The product was recrystallized from ethanol to give 0.2 g of thiooxamide **3c** (62%), m.p. 142—143 °C. Found (%): C, 57.73; H, 5.64; N, 13.57. $C_{10}H_{12}N_2OS$. Calculated (%): C, 57.69; H, 5.77; N, 13.46. ^{1}H NMR, δ: 3.75 (s, 6 H, Me); 7.10 (m, 1 H, H arom.); 7.30, 7.70 (both m, each 2 H, H arom.); 9.65 (s, 1 H, NH). MS, *m/z*: 208 $[M]^+$.

Synthesis of monothiooxamides (general procedure *A*). Chloroacetamide **1** (5.0 mmol) was added to a solution of an amine (5.5 mmol) and sulfur (0.7 g) in 10 mL of DMF prepared beforehand. The reaction mixture was stirred at ≈20 °C for 8 h, cooled, and diluted with water. The precipitate was filtered off, washed with water, and dried. The product was dissolved in acetone (10 mL) and the solution was filtered. The residue after the removal of acetone was recrystallized from 95% ethanol to give thiooxamide **3a**, 88%, m.p. 58—60 °C (*cf.* Ref. 7: 58—60 °C) and thiooxamide **3b**, 92%, m.p. 165—166 °C (*cf.* Ref. 6: 166 °C).

***N*(S)-[2-(2-Chloro-4-nitrophenylamino)ethyl]-*N*(O)-phenylthiooxamide (3d).** Yield 53%, m.p. 166—168 °C. Found (%): C, 50.77; H, 3.89; Cl, 3.27; N, 14.86. $C_{16}H_{15}ClN_4O_3S$. Calculated (%): C, 50.73; H, 3.99; Cl, 9.36; N, 14.79. ^{1}H NMR, δ: 3.65, 3.90 (both m, each 2 H, CH_2); 7.00 (m, 2 H, H arom.); 7.15 (t, 1 H, H arom., J = 7.3 Hz); 7.40, 7.65 (both m, each 2 H, H arom.); 8.05 (m, 1 H, NH); 8.10 (s, 1 H, H arom.); 10.35, 11.10 (both s, each 1 H, NH).

***N*(S),*N*(S)-Diethyl-*N*(O)-[3,5-di(trifluoromethyl)phenyl]thiooxamide (3e).** Yield 86%, m.p. 100—101 °C. Found (%): C, 45.29; H, 3.63; F, 30.56; N, 7.62. $C_{14}H_{14}F_6N_2OS$. Calculated (%): C, 45.16; H, 3.76; F, 30.64; N, 7.53. ^{1}H NMR, δ: 1.25 (m, 6 H, Me); 3.55, 3.95 (both m, each 2 H, CH_2); 7.80 (m, 1 H, H arom.); 8.30 (m, 2 H, H arom.); 11.15 (s, 1 H, NH). MS, *m/z*: 372 $[M]^+$.

***N*-(3-Nitrophenyl)-2-piperidino-2-thioxoacetamide (3f).** Yield 78%, m.p. 165—167 °C (*cf.* Ref. 10: 165—167 °C).

***N*-(3,4-Dichlorophenyl)-2-piperidino-2-thioxoacetamide (3g).** Yield 73%, m.p. 186—187 °C (*cf.* Ref. 10: 185—187 °C).

***N*-(2-Chloropyridin-3-yl)-2-morpholino-2-thioxoacetamide (3h).** Yield 68%, m.p. 157—159 °C. Found (%): C, 46.20; H, 4.30; Cl, 12.36; N, 14.61. $C_{11}H_{12}ClN_3O_2S$. Calculated (%): C, 46.24; H, 4.23; Cl, 12.41; N, 14.70. ^{1}H NMR, δ: 3.78 (m, 6 H, H morphol.); 4.15 (m, 2 H, morphol.); 7.50 (m, 1 H, Py); 8.15 (d, 1 H, Py, J = 7.8 Hz); 8.30 (m, 1 H, Py); 11.50 (s, 1 H, NH).

***N*-(3-Cyano-5,6-dihydro-4*H*-cyclopenta[*b*]thien-2-yl)-2-morpholino-2-thioxoacetamide (3i).** Yield 65%, m.p. 217—219 °C. Found (%): C, 61.17; H, 5.32; N, 10.22. $C_{14}H_{15}N_2O_2S_2$. Calculated (%): C, 61.09; H, 5.45; N, 10.18. ^{1}H NMR, δ: 2.35, 2.75, 2.85 (all m, each 2 H, CH_2); 3.60, 3.70, 3.80, 4.15 (all m, each 2 H, H morphol.); 12.25 (s, 1 H, NH). MS, *m/z*: 307 $[M]^+$.

***N*,*N*′-Bis[(2-morpholino-1-oxo-2-thioxo)ethyl]-1,2-phenylenediamine (5b).** Yield 72%, m.p. 229—231 °C. Found (%): C, 51.17; H, 5.25; N, 13.26. $C_{18}H_{22}N_4O_4S_2$. Calculated (%): C, 51.04; H, 5.41; N, 13.29. ^{1}H NMR, δ: 3.65—3.85 (m, 12 H, H morphol.); 4.15 (m, 4 H, H morphol.); 7.30, 7.65 (both m, each 2 H, H arom.); 9.95 (s, 2 H, NH). MS, *m/z*: 422 $[M]^+$.

***N,N′*-Bis[2-(2,6-dimethylanilino-2-oxo-1-thioxo)ethyl]piperazine (8a).** Yield 56%, m.p. 294—297 °C. Found (%): C, 61.58; H, 6.09; N, 12.05. $C_{24}H_{28}N_4O_2S_2$. Calculated (%): C, 61.51; H, 6.02; N, 11.96. ^{1}H NMR, δ: 2.25, 2.30 (both s, each 6 H, Me); 4.05—4.18, 4.20—4.38 (both m, each 4 H, CH_2); 7.10 (m, 6 H, H arom.); 10.00 (s, 2 H, NH). MS, *m/z*: 469 $[M]^+$.

***N*(S)-(Adamant-1-yl)-*N*(O)-phenylthiooxamide (8b).** Yield 64%, m.p. 135—139 °C. Found (%): C, 68.83; H, 6.95; N, 8.85. $C_{18}H_{22}N_2OS$. Calculated (%): C, 68.75; H, 7.05; N, 8.91. ^{1}H NMR, δ: 1.51—1.75 (m, 7 H, Ad); 2.15 (m, 3 H, Ad); 2.35 (m, 5 H, Ad); 7.15 (t, 1 H, H arom., J = 7.5 Hz); 7.38 (d, 2 H, H arom., J = 7.7 Hz); 7.72 (d, 2 H, H arom., J = 7.9 Hz); 9.78, 10.38 (both s, each 1 H, NH). MS, *m/z*: 314 $[M]^+$.

***N*(S)-Cyclopropyl-*N*(O)-phenylthiooxamide (8d).** Yield 48%, m.p. 93—95 °C (*cf.* Ref. 10: 93—95 °C).

***N*(S)-Allyl-*N*(O)-phenylthiooxamide (8e).** Yield 67%, m.p. 85—86 °C (*cf.* Ref. 10: 84—86 °C).

***N*(O)-(2,6-dibromo-4-methylphenyl)thiooxamide (8h).** Yield 82%, m.p. 174—176 °C. Found (%): C, 44.69; H, 3.67; Br, 35.12; N, 6.07. $C_{17}H_{16}Br_2N_2OS$. Calculated (%): C, 44.76; H, 3.54; Br, 35.03; N, 6.14. ^{1}H NMR, δ: 2.35 (s, 3 H, Me); 3.00, 3.85 (both m, each 2 H, CH_2); 7.20—7.40 (m, 5 H, H arom.); 7.58 (s, 2 H, H arom.); 10.25, 10.90 (both s, each 1 H, NH).

Synthesis of monothiooxamide (general procedure *B*). Chloroacetamide **1** (5.0 mmol) was added to a mixture, prepared beforehand, consisting of an aromatic amine (5.5 mmol), sulfur (0.7 g), and triethylamine (1 mL) in 5 mL of DMF. The mixture was stirred at ≈20 °C for 8 h, cooled, and diluted with water. The precipitate was filtered off, washed with water, and dried in air. The product was dissolved in acetone, the solution was filtered, and the residue remaining after removal of acetone from the filtrate was recrystallized from 95% ethanol.

***N,N′*-Bis[(2-anilino-1-oxo-2-thioxo)ethyl]-1,2-phenylenediamine (5a).** Yield 61%, m.p. 225—227 °C. Found (%): C, 60.87; H, 4.07; N, 12.93. $C_{22}H_{18}N_4O_2S_2$. Calculated (%): C, 60.81; H, 4.18; N, 12.89. ^{1}H NMR, δ: 7.35, 7.45 (both m, each 4 H, H arom.); 7.75 (m, 2 H, H arom.); 7.95 (m, 4 H, H arom.); 10.60, 12.30 (both s, each 2 H, NH). MS, *m/z*: 434 $[M]^+$.

***N*(S)-(4-Methoxycarbonylphenyl)-*N*(O)-phenylthiooxamide (6a).** Yield 58%, m.p. 166—167 °C. Found (%): C, 61.42; H, 4.66; N, 9.03. $C_{16}H_{14}N_2O_3S$. Calculated (%): C, 61.13; H, 4.49; N, 8.91. ^{1}H NMR, δ: 3.90 (s, 3 H, Me); 7.20 (m, 1 H, H arom.); 7.40, 7.80, 8.05, 8.20 (all m, each 2 H, H arom.); 10.50, 12.50 (both s, each 1 H, NH). MS, *m/z*: 314 $[M]^+$.

***N*(S)-[4-(Acetylamino)phenyl]-*N*(O)-phenylthiooxamide (6b).** Yield 68%, m.p. 205—208 °C. Found (%): C, 61.42; H, 4.66; N, 14.01. $C_{16}H_{15}N_3O_2S$. Calculated (%): C, 61.32; H, 4.82; N, 13.41. ^{1}H NMR, δ: 2.10 (s, 3 H, Me); 7.20 (m, 1 H, H arom.); 7.40 (d, 2 H, H arom., J = 7.1 Hz); 7.65 (d, 2 H, H arom., J = 8.0 Hz); 7.80 (d, 2 H, H arom., J = 7.0 Hz); 7.95 (d, 2 H, H arom., J = 7.6 Hz); 10.00, 10.45, 12.50 (all s, each 1 H, NH).

***N*(S)-[4-(Diethylamino)phenyl]-*N*(O)-phenylthiooxamide (6c).** Yield 53%, m.p. 108—109 °C. Found (%): C, 66.36; H, 6.14; N, 12.96. $C_{18}H_{21}N_3OS$. Calculated (%): C, 66.03; H, 6.46; N, 12.83. ^{1}H NMR, δ: 1.15 (m, 6 H, Me); 3.55 (m, 4 H, CH_2); 6.80 (m, 2 H, H arom.); 7.20 (m, 1 H, H arom.); 7.45, 7.80, 7.95 (all m, each 2 H, H arom.); 10.50, 12.05 (both s, each 1 H, NH). MS, *m/z*: 327 $[M]^+$.

***N*(O)-(2-Cyanophenyl)-*N*(S)-(4-methoxyphenyl)thiooxamide (6d).** Yield 62%, m.p. 174—175 °C. Found (%): C, 61.51; H, 4.27; N, 13.12. $C_{16}H_{13}N_3O_2S$. Calculated (%): C, 61.72; H, 4.21; N, 13.50. ^{1}H NMR, δ: 3.85 (s, 3 H, Me); 7.05 (d, 2 H, H arom., J = 8.9 Hz); 7.45, 7.80 (both t, each 1 H, H arom., J = 7.7 Hz); 7.92 (m, 3 H, H arom.); 8.10 (d, 1 H, H arom., J = 8.3 Hz); 10.90, 12.33 (both s, each 1 H, NH).

***N*(O),*N*(S)-Bis(4-chlorophenyl)thiooxamide (6e).** Yield 73%, m.p. 155—158 °C. Found (%): C, 51.98; H, 3.03; C1, 21.63; N, 9.02. $C_{14}H_{10}Cl_2N_2OS$. Calculated (%): C, 51.71; H, 3.10; Cl, 21.80; N, 8.61. ^{1}H NMR, δ: 7.45, 7.55 (both d, each 2 H, H arom., J = 8.8 Hz); 7.85, 8.00 (both d, each 2 H, H arom., J = 8.8 Hz); 10.60, 12.40 (both s, each 1 H, NH).

***N*(O)-[4-(Methoxycarbonyl)phenyl]-*N*(S)-phenylthiooxamide (6f).** Yield 57%, m.p. 171—174 °C. Found (%): C, 61.42; H, 4.66; N, 9.03. $C_{16}H_{14}N_2O_3S$. Calculated (%): C, 61.13; H, 4.49; N, 8.91. ^{1}H NMR, δ: 3.85 (s, 3 H, Me); 7.35 (t, 1 H, H arom., J = 8.1 Hz); 7.95 (m, 2 H, H arom.); 8.00 (m, 6 H, H arom.); 10.80, 12.40 (both s, each 1 H, NH). MS, *m/z*: 314 $[M]^+$.

***N*(S)-(1-Naphthyl)thiooxamide (6g).** Yield 67%, m.p. 198—200 °C. Found (%): C, 62.78; H, 4.16; N, 12.38. $C_{12}H_{10}N_2OS$. Calculated (%): C, 62.59; H, 4.38; N, 12.16. ^{1}H NMR, δ: 7.55 (m, 4 H, H arom.); 7.72 (m, 1 H, H arom.); 8.00 (m, 2 H, H arom.); 8.15 (m, 2 H, NH_2); 12.35 (s, 1 H, NH). MS, *m/z*: 230 $[M]^+$.

***N*(S)-(2-Pyridyl)thiooxamide (7a).** Yield 77%, m.p. 160—162 °C. Found (%): C, 46.66; H, 3.76; N, 23.23. $C_7H_7N_3OS$. Calculated (%): C, 46.40; H, 3.89; N, 23.19. ^{1}H NMR, δ: 7.40 (m, 1 H, Py); 8.00 (t, 1 H, Py, J = 7.7 Hz); 8.25 (s, 2 H, NH_2); 8.55 (m, 1 H, Py); 8.82 (d, 1 H, Py, J = 8.2 Hz); 11.80 (s, 1 H, NH). MS, *m/z*: 181 $[M]^+$.

***N*(S)-[2-(6-Bromopyridyl)]thiooxamide (7b).** Yield 67%, m.p. 195—198 °C. Found (%): C, 32.28; H, 2.36; Br, 30.84; N, 16.07. $C_7H_6BrN_3OS$. Calculated (%): C, 32.32; H, 2.33; Br, 30.72; N, 16.15. ^{1}H NMR, δ: 8.20 (m, 3 H, Py); 8.65 (m, 2 H, NH_2); 11.95 (s, 1 H, NH).

***N*(S)-(4-Pyridyl)thiooxamide (7c).** Yield 35%, m.p. 210—212 °C. Found (%): C, 46.37; H, 3.92; N, 23.23. $C_7H_7N_3OS$. Calculated (%): C, 46.40; H, 3.89; N, 23.19. ^{1}H NMR, δ: 8.12 (m, 4 H, Py); 8.65 (m, 2 H, NH_2); 12.25 (s, 1 H, NH). MS, *m/z*: 181 $[M]^+$.

***N*(S)-(3-Carbamoyl-4,5,6,7-tetrahydro-1-benzothiophen-2-yl)thiooxamide (7d).** Yield 58%, m.p. 218—224 °C. Found (%): C, 46.76; H, 4.06; N, 14.86. $C_{11}H_{13}N_3O_2S_2$. Calculated (%): C, 46.62; H, 4.62; N, 14.83. ^{1}H NMR, δ: 2.80 (m, 4 H, $-CH_2CH_2-$); 2.65—2.90 (m, 4 H, 2 CH_2); 7.50, 8.10 (both m, each 2 H, NH_2); 14.5 (s, 1 H, NH). MS, *m/z*: 283 $[M]^+$.

***N*(S)-(2-Bromophenyl)thiooxamide (8c).** Yield 76%, m.p. 188—190 °C. Found (%): C, 37.02; H, 2.97; Br, 30.90; N, 10.73. $C_8H_7BrN_2OS$. Calculated (%): C, 37.08; H, 2.72; Br, 30.84; N, 10.81. ^{1}H NMR, δ: 7.30 (t, 1 H, H arom., J = 7.8 Hz); 7.45 (t, 1 H, H arom., J = 7.7 Hz); 7.75 (m, 2 H, H arom.); 8.15 (m, 2 H, NH_2); 12.00 (s, 1 H, NH).

2-(2-Benzoyl-3-phenylaziridino)-2-thioxoacetamide (8f). Yield 42%, m.p. 92—94 °C. Found (%): C, 65.82; H, 4.50; N, 9.44. $C_{17}H_{14}N_2O_2S$. Calculated (%): C, 65.79; H, 4.55; N, 9.03. ^{1}H NMR, δ: 3.20, 3.75 (both m, each 1 H, CH); 7.25—7.75 (m, 10 H, H arom.); 8.05 (m, 2 H, NH_2).

***N*(S)-(2,6-Dimethylphenyl)-*N*(O)-(4-nitrophenyl)thioxoacetamide (8g).** Yield 64%, m.p. 190—192 °C. Found (%):

C, 58.39; H, 4.56; N, 12.78. $C_{16}H_{15}N_3O_3S$. Calculated (%): C, 58.35; H, 4.59; N, 12.67. ^{1}H NMR, δ: 2.20 (s, 6 H, Me); 7.20 (m, 3 H, H arom.); 8.15, 8.35 (both d, each 2 H, H arom., J = 9.2 Hz); 11.00, 12.22 (both s, each 1 H, NH). MS, m/z: 329 $[M]^+$.

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