Synthesis and reactivity of monothiooxamides of the aminonitroarene series*

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Monothiooxamides containing aminonitrobenzene and aminonitropyridine fragments have been synthesized. A possibility to synthesize thioesters and fused imidazole and diazepine derivatives on their basis has been demonstrated.

Key words: thiooxamides, α-chloroacetamides, dibenzodiazepines, benzimidazoles, thioesters, sulfur.

Earlier, we have suggested methods for preparing a number of monothiooxamides and studied their reactivity.[1]

Monothiooxamide nitro derivatives are of significant interest due to the fact that many bioactive compounds contain a nitro group, which can be also used in various transformations, including heterocyclization reactions.

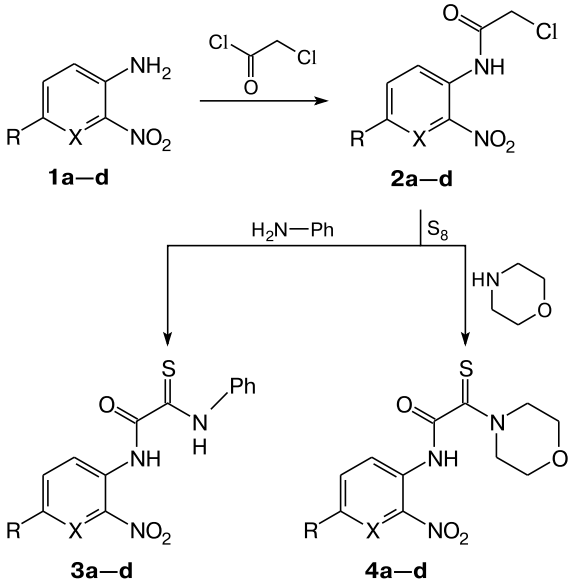
The purpose of our work consisted in the synthesis of new monothiooxamides of the aminonitrobenzene and aminonitropyridine series and design of benzimidazole and dibenzodiazepine derivatives on their basis.

The monothiooxamides were synthesized based on aromatic vicinal nitro amines **1a—d** using a method developed by us earlier[1] consisting in the reaction of α-chloroacetamides with pre-prepared solution of sulfur in amines.

The starting chloroacetamides **2a—d** were obtained by the reaction of chloroacetyl chloride with aminonitrobenzenes **1a—c** and aminonitropyridine **1d** in dimethylformamide. The nitro group does not affect the acylation process, the reaction proceeds smoothly in quantitative yield (Scheme 1).

A pre-prepared solution of elementary sulfur in amines kept for 30 min was used in the S-functionalization reactions of chloroacetamides. The process smoothly proceeds at room temperature with morpholine; when weaker base (aniline) has been used, the addition of triethylamine or pyridine was necessary (see Scheme 1).

Scheme 1



Compound	R	X
a	H	CH
b	Cl	CH
c	Me	CH
d	H	N

* Dedicated to Academician O. N. Chupakhin on the occasion of his 75th birthday.

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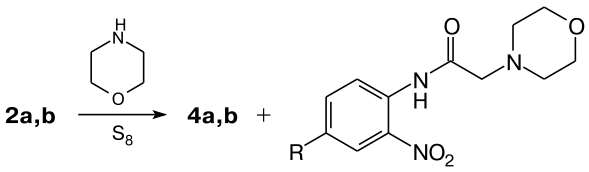
When all the components were mixed simultaneously, the reaction is not that smooth and, along with monothiooxamides **4a,b**, there are formed amines **5a,b** in the ratio 1 : 5, respectively (Scheme 2).

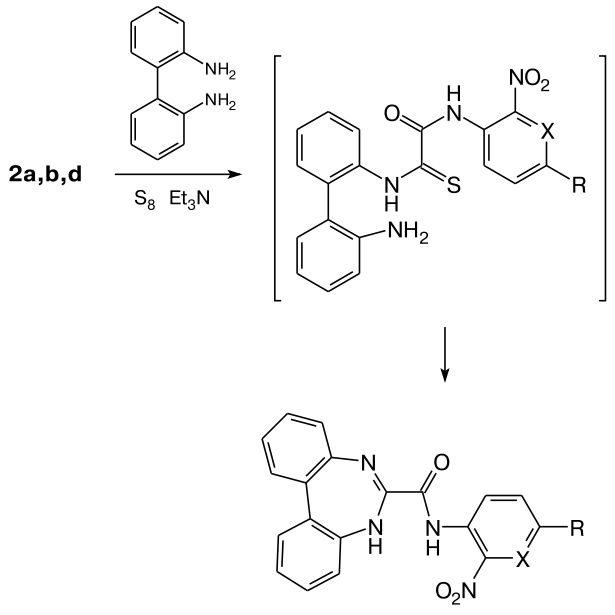
Scheme 2



Thus, the sulfurization of nitro derivatives proceeds similarly to the reactions with chloroacetamides described by us earlier[1] and can be used in designing heterocyclic compounds.

We have shown that the reaction of chloroacetamides **2a,b,d** with a pre-prepared mixture of diphenyl-2,2′-diamine, triethylamine, and elementary sulfur leads to carbamoyl-containing 5*H*-dibenzo[*d*,*f*][1,3]diazepines **6a,b,d**. The process apparently proceeds through the formation of monothiooxamides, which then are converted to dibenzodiazepines (Scheme 3).

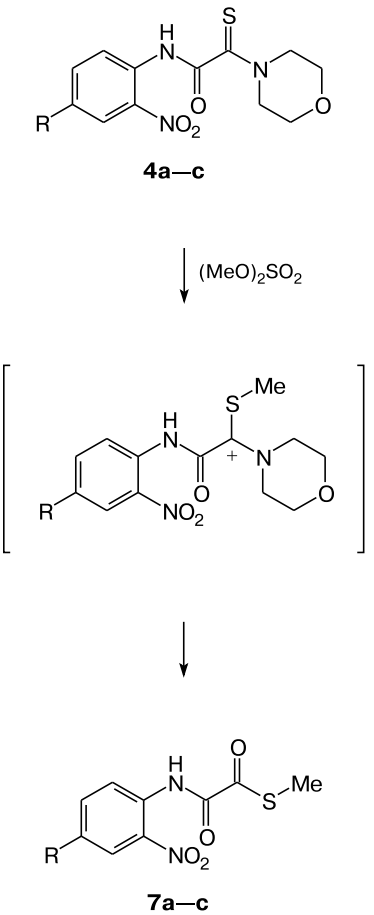
Scheme 3



Compound	a	b	d
R	H	Cl	H
X	CH	CH	N

Modification of thioamide and nitro groups in the monothiooxamide derivatives obtained allows one to synthesize various compounds. Note that the nitro group in monothiooxamides **4a—c** does not considerably affect the nucleophilicity of the thiocarbonyl group, which is confirmed, in particular, by a possibility to obtain monothiooxamic S-esters **7a—c** from monothiooxamides. The former were synthesized by the reaction of monothiooxamides with dimethyl sulfate and subsequent treatment of isothioamides formed with water (Scheme 4).

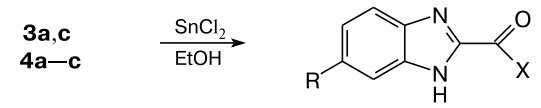
Scheme 4



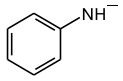
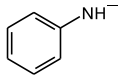
Reduction of the nitro groups in *ortho*-position to the monothiooxamide fragment leads to the heterocyclization with the formation of imidazole ring (Scheme 5).

In conclusion, the nitro group in monothiooxamides creates additional possibilities for the synthesis of various derivatives and can be involved into the heterocyclization reaction.

Scheme 5



8a,c
9a—c

Compound	R	X
8a	H	
8c	Me	
9a	H	
9b	Cl	
9c	Me	

Experimental

^{1}H NMR spectra were recorded on a Bruker WM-200 (200 MHz) and Bruker WM-250 (250 MHz) spectrometers in DMSO-d_6. Mass spectra were obtained on a Varian MAT CH-6 instrument with direct inlet of the sample into the ion source, the energy of ionization, 70 eV, directing potential, 1.75 kV. Melting points were determined on a Boetius heating stage and are uncorrected. Analysis of reaction mixtures and monitoring of isolated product purities were performed by TLC on Merck UV-254 plates.

***N*-(2-Nitrophenyl)-2-chloroacetamide (2a).** Chloroacetyl chloride (0.4 mL (4.8 mmol) was slowly added to amine **1a** (0.5 g, 4 mmol) in DMF (3 mL) with stirring and ice-cooling in such a way that to keep temperature below 5—7 °C, then, the mixture was stirred for 1.5 h, poured into water, a precipitate formed was filtered off to obtain compound **2a** (0.76 g, 98%), m.p. 109—111 °C (agrees with the data in Ref. 2). ^{1}H NMR, δ: 4.33 (s, 2 H, CH_2); 7.60 (m, 2 H, Ar); 7.78 (m, 1 H, Ar); 8.80 (m, 1 H, Ar); 11.6 (s, 1 H, NH). MS, *m/z*: 214 $[M]^+$. Found (%): C, 44.67; H, 3.35; N, 13.10; Cl, 16.58. $C_8H_7ClN_2O_3$. Calculated (%): C, 44.77; H, 3.29; N, 13.05; Cl, 16.52.

***N*-(4-Chloro-2-nitrophenyl)-2-chloroacetamide (2b)** was obtained from **1b** (0.5 g, 2.9 mmol) similarly to compound **2a**, the yield was 0.68 g (97%), m.p. 140—141 °C (agrees with the data in Ref. 3). ^{1}H NMR, δ: 4.30 (s, 2 H, CH_2); 7.30 (m, 1 H, Ar); 8.35 (m, 1 H, Ar); 8.60 (m, 1 H, Ar); 11.35 (s, 1 H, NH). MS, *m/z*: 249 $[M]^+$. Found (%): C, 38.62; H, 2.50; N, 11.16; Cl, 28.50. $C_8H_6Cl_2N_2O_3$. Calculated (%): C, 38.58; H, 2.43; N, 11.25; Cl, 28.47.

***N*-(4-Methyl-2-nitrophenyl)-2-chloroacetamide (2c)** was obtained from **1c** (0.5 g, 3.3 mmol) similarly to compound **2a**, the yield was 0.72 g (96%), m.p. 199—121 °C (agrees with the data in Ref. 4). ^{1}H NMR, δ: 2.4 (s, 3 H, CH_3); 4.35 (s, 2 H, CH_2); 7.55 (d, 1 H, Ar, J = 8.36 Hz); 7.65 (d, 1 H, Ar, J = 8.3 Hz); 7.85 (s, 1 H, Ar); 10.55 (s, 1 H, NH). MS, *m/z*: 229 $[M]^+$. Found (%): C, 47.34; H, 3.82; N, 12.20; Cl, 15.48. $C_9H_9ClN_2O_3$. Calculated (%): C, 47.28; H, 3.97; N, 12.25; Cl, 15.51.

***N*-(2-Nitropyridin-3-yl)-2-chloroacetamide (2d)** was obtained from **1d** (0.5 g, 3,6 mmol) similarly to compound **2a**, the yield was 0.73 g (95%), m.p. 178—179 °C. ^{1}H NMR, δ: 4.38 (s, 2 H, CH_2); 7.85 (m, 1 H, Py); 8.30 (m, 1 H, Py); 8.42 (m, 1 H, Py,); 10.68 (s, 1 H, NH). MS, *m/z*: 215 $[M]^+$. Found (%): C, 39.06; H, 2.80; N, 19.43; Cl, 16.48. $C_7H_6ClN_3O_3$. Calculated (%): C, 39.00; H, 2.81; N, 19.49; Cl, 16.44.

***N*-(2-Nitrophenyl)-2-phenylamino-2-thioxoacetamide (3a).** Chloroacetanilide **2a** (0.1 g, 0.47 mmol) was added to a suspension of sulfur (0.045 g, 1,4 mmol), amine (aniline or morpholine, 0.94 mmol), triethylamine (in the case of aniline, 0.94 mmol) in DMF (1 mL) that has been kept for 30 min. The reaction mixture was stirred for 7 h at room temperature, then the mixture was poured into water, a precipitate was filtered off. To purify the product from unreacted sulfur, it was dissolved in acetone, the acetone solution was separated, the solvent was evaporated *in vacuo*. The solid residue was recrystallized from ethanol to obtain compound **3a** (0.13 g, 93%), m.p. 158—160 °C. ^{1}H NMR, δ: 7.34 (m, 1 H, Ar); 7.46 (m, 3 H, Ar); 7.90 (m, 3 H, Ar); 8.22 (d, 1 H, Ar, J = 8.41 Hz); 8.51 (d, 1 H, Ar, J = 8,31 Hz); 12.10 (s, 1 H, NH); 12.45 (s, 1 H, NH). MS, *m/z*: 301 $[M]^+$. Found(%): C, 55.65; H, 3.74; N, 13.80; S, 10.85. $C_{14}H_{11}N_3O_3S$. Calculated (%): C, 55.80; H, 3.68; N, 13.95; S, 10.64.

***N*-(4-Chloro-2-nitrophenyl)-2-phenylamino-2-thioxoacetamide (3b)** was obtained from **2b** (0.1 g, 0.4 mmol) similarly to compound **3a**, the yield was 0.12 g (90%), m.p. 161—163 °C. ^{1}H NMR, δ: 7.30 (m, 1 H, Ar); 7.56 (m, 3 H, Ar); 7.65 (m, 2 H, Ar); 8.16 (m, 1 H, Ar); 8.60 (d, 1 H, Ar, J = 8.26 Hz); 11.95 (s, 1 H, NH); 12.3 (s, 1 H, NH). MS, *m/z*: 335 $[M]^+$. Found (%): C, 50.15; H, 2.87; N, 12.42; S, 9.60; Cl, 10.55. $C_{14}H_{10}ClN_3O_3S$. Calculated (%): C, 50.08; H, 3.00; N, 12.51; S, 9.55; Cl, 10.56.

***N*-(4-Methyl-2-nitrophenyl)-2-phenylamino-2-thioxoacetamide (3c)** was obtained from **2c** (0.1 g, 4.4 mmol) similarly to compound **3a**, the yield was 0.11 g (80%), m.p. 111—113 °C. ^{1}H NMR, δ: 2.37 (s, 3 H, CH_3); 7.32 (m, 1 H, Ar); 7.45 (m, 3 H, Ar); 7.68 (m, 2 H, Ar); 8.10 (m, 2 H, Ar); 12.05 (s, 1 H, NH); 12.40 (s, 1 H, NH). MS, *m/z*: 315 $[M]^+$. Found (%): C, 57.33; H, 3.99; N, 13.40; S, 10.12. $C_{15}H_{13}N_3O_3S$. Calculated (%): C, 57.13; H, 4.16; N, 13.33; S, 10.17.

***N*-(2-Nitropyridin-3-yl)-2-phenylamino-2-thioxoacetamide (3d)** was obtained from **2d** (0.1 g, 4.6 mmol) similarly to compound **3a**, the yield was 0.09 g (65%), m.p. 163—165 °C. ^{1}H NMR, δ: 7.39 (d, 1 H, Ar, J = 7.27 Hz); 7.46 (t, 2 H, Ar, J = 7.24 Hz); 7.90 (m, 2 H, Ar); 7.95 (m, 1 H, Py); 8.45 (m, 1 H, Py); 8.79 (d, 1 H, Py, J = 8.02 Hz); 11.85 (s, 1 H, NH); 12.50 (s, 1 H, NH). MS, *m/z*: 302 $[M]^+$. Found (%): C, 51.54; H, 3.26; N, 18.63; S, 10.83. $C_{13}H_{10}N_4O_3S$. Calculated (%): C, 51.65; H, 3.33; N, 18.53; S, 10.61.

***N*-(2-Nitrophenyl)-2-morpholino-2-thioxoacetamide (4a)** was obtained from **2a** (0.1 g, 0.47 mmol) similarly to compound **3a**, the yield was 0.1 g (70%), m.p. 137—138 °C (agrees with the data in Ref. 5). ^{1}H NMR, δ: 3.8 (m, 6 H, CH_2); 4.15 (m, 2 H, CH_2) ; 7.5 (m, 1 H, Ar); 7.75 (m, 2 H, Ar); 8.0 (d, 1 H, Ar J = 8.13 Hz); 11.0 (s, 1 H, NH). MS, *m/z*: 295 $[M]^+$. Found (%): C, 48.61; H, 4.56; N, 14.35; S, 10.74. $C_{12}H_{13}N_3O_4S$. Calculated (%): C, 48.80; H, 4.44; N, 14.23; S, 10.86.

***N*-(4-Chloro-2-nitrophenyl)-2-morpholino-2-thioxoacetamide (4b)** was obtained from **2b** (0.1 g, 0.4 mmol) similarly to

compound **3a**, the yield was 0.1 g (80 %), m.p. 155—156 °C. ^{1}H NMR, δ: 3.75 (m, 6 H, CH_2); 4.15 (d, 2 H, CH_2, J = 8.34 Hz); 7.74 (d, 1 H, Ar, J = 8.74 Hz); 7.85 (d, 1 H, Ar, J = 8.71 Hz); 8.15 (s, 1 H, Ar); 11.0 (s, 1 H, NH). MS, m/z: 329 $[M]^+$. Found (%): C, 43.61; H, 3.52; N, 12.8; S, 9.91; Cl, 10.6. $C_{12}H_{12}ClN_3O_4S$. Calculated (%): C, 43.71; H, 3.67; N, 12.74; S, 9.72; Cl, 10.75.

***N*-(4-Methyl-2-nitrophenyl)-2-morpholino-2-thioxoacetamide (4c)** was obtained from **2c** (0.1 g, 4.4 mmol) similarly to compound **3a**, the yield was 0.1 g (80%), m.p. 150—152 °C. ^{1}H NMR, δ: 2.4 (s, 3 H, CH_3); 3.75 (m, 6 H, CH_2); 4.15 (s, 2 H, CH_2); 7.65 (t, 2 H, Ar, J = 7.98 Hz); 7.85 (s, 1 H, Ar); 10.85 (s, 1 H, NH). MS, m/z: 309 $[M]^+$. Found (%): C, 50.36; H, 4.98; N, 13.43; S, 10.6. $C_{13}H_{15}N_3O_4S$. Calculated (%): C, 50.47; H, 4.89; N, 13.58; S, 10.37.

***N*-(2-Nitropyridin-3-yl)-2-morpholino-2-thioxoacetamide (4d)** was obtained from **2d** (0.1 g, 4.6 mmol) similarly to compound **3a**, the yield was 0.08 g (60%), m.p. 159—161 °C. ^{1}H NMR, δ: 3.75 (t, 6 H, CH_2, J = 10.35 Hz); 4.15 (t, 2 H, CH_2, J = 9.63 Hz); 7.87 (m, 1 H, Py); 8.25 (d, 1 H, Py, J = 8.1 Hz); 8.45 (m, 1 H, Py); 11.15 (s, 1 H, NH). MS, m/z: 296 $[M]^+$. Found (%): C, 44.43; H, 3.87; N, 18.99; S, 10.89. $C_{11}H_{12}N_4O_4S$. Calculated (%): C, 44.59; H, 4.08; N, 18.91; S, 10.82.

***N*-(2-Nitrophenyl)-2-morpholinoacetamide (5a).** Chloroacetanilide **2a** (0.25 g, 1.2 mmol) in DMF (2 mL) was added to a mixture of sulfur (0.1 g, 3.6 mmol) and morpholine (1.3 mmol). The reaction mixture was stirred for 4 h at room temperature (TLC monitoring showed formation of a mixture of products **4a** and **5a**). Then the mixture was poured into water, a precipitate was filtered off; to purify from the unreacted sulfur, the residue was dissolved in acetone, the acetone solution was separated, the solvent was evaporated *in vacuo*. The mixture of products obtained was separated by preparative TLC (eluent, light petroleum—ethyl acetate, 3 : 1) to obtain compound **4a** (0.05 g, 14%), m.p. 137—138 °C, MS, m/z: 295 $[M]^+$ and compound **5a** (0.26 g, 82%), m.p. 133—135 °C (agrees with the data in Ref. 6). ^{1}H NMR, δ: 2.1 (s, 2 H, CH_2); 2.4 (s, 2 H, CH_2); 3.2 (s, 2 H, CH_2); 3.7 (d, 4 H, CH_2, J = 3.72 Hz); 7.30 (t, 1 H, Ar, J = 7.59 Hz); 7.8 (t, 1 H, Ar, J = 7.55 Hz); 8.2 (d, 1 H, Ar, J = 8.23 Hz); 8.6 (d, 1 H, Ar, J = 8.26 Hz); 11.5 (s, 1 H, NH). MS, m/z: 265 $[M]^+$. Found (%): C, 54.21; H, 5.75; N, 15.76. $C_{12}H_{15}N_3O_4$. Calculated (%): C, 54.33; H, 5.70; N, 15.84.

***N*-(4-Chloro-2-nitrophenyl)-2-morpholinoacetamide (5b)** was obtained from **2b** (0.25 g, 1 mmol) similarly to compound **5a**. There were isolated compound **4b** (0.06 g, 18%), m.p. 155—156 °C, MS, m/z: 329 $[M]^+$ and compound **5b** (0.24 g, 80%), m.p. 265—267 °C. ^{1}H NMR, δ: 3.21 (s, 2 H, CH_2); 3.70 (s, 4 H, CH_2); 3.95 (s, 4 H, CH_2); 7.20 (m, 2 H, Ar); 7.40 (m, 1 H, Ar); 12.18 (s, 1 H, NH). MS, m/z: 300 $[M]^+$. Found (%): C, 47,89; H, 4,86; N, 14.17. $C_{12}H_{14}ClN_3O_4$. Calculated (%): C, 48.09; H, 4.71; N, 14.02.

***N*-(2-Nitrophenyl)-5*H*-dibenzo[*d*,*f*][1,3]diazepin-6-carboxamide (6a).** A suspension of 2,2′-diaminobiphenyl (0.22 g, 1.2 mmol), sulfur (0.19 g, 6 mmol), triethylamine (0.3 g, 3 mmol) in DMF (5 mL) was stirred at room temperature for 20 min, followed by addition of chloroacetanilide **2a** (0.21 g, 1 mmol). The reaction mixture was heated for 6 h at 60—70 °C, cooled to room temperatures, poured into water (100 mL), a precipitate was filtered off, dissolved in acetone, and concentrated *in vacuo*. The residue was recrystallized from ethanol or purified by column chromatography in the ethyl acetate—hexane (1 : 3) solvent system to obtain compound **6a** (0.23 g, 65%), m.p. 233—235 °C. ^{1}H NMR, δ: 7.05 (d, 2 H, Ar, J = 7.67 Hz); 7.15 (m, 3 H, Ar); 7.3 (m, 3 H, Ar); 7.45 (m, 1 H, Ar); 7.85 (m, 1 H, Ar); 8.2 (d, 1 H, Ar, J = 8.14 Hz); 8.65 (d, 1 H, Ar, J = 8.38 Hz); 9.8 (s, 1 H, NH); 10.4 (s, 1 H, NH). MS, m/z: 358 $[M]^+$. Found (%): C, 67.20; H, 3.85; N, 15.69. $C_{20}H_{14}N_4O_3$. Calculated (%): C, 67.03; H, 3.94; N, 15.63.

***N*-(4-Chloro-2-nitrophenyl)-5*H*-dibenzo[*d*,*f*][1,3]diazepin-6-carboxamide (6b)** was obtained from **2b** (0.25 g, 1 mmol) similarly to compound **6a**. The yield was 0.26 g (66%), m.p. 220—222 °C. ^{1}H NMR, δ: 7.05 (d, 2 H, Ar, J = 0.026 Hz); 7.2 (t, 2 H, Ar, J = 0.024 Hz); 7.35 (d, 3 H, Ar, J = 0.025 Hz); 7.4 (d, 2 H, Ar, J = 0.026 Hz); 7.9 (m, 1 H, Ar); 8.25 (m, 1 H, Ar); 9.95 (s, 1 H, NH); 10.35 (s, 1 H, NH). MS, m/z: 393$[M]^+$. Found (%): C, 61.04; H, 3.47; N, 14.20; Cl, 9.16. $C_{20}H_{13}ClN_4O_3$. Calculated (%): C, 61.16; H, 3.34; N, 14.26; Cl, 9.03.

***N*-(2-Nitropyridin-3-yl)-5*H*-dibenzo[*d*,*f*][1,3]diazepine-6-carboxamide (6c)** was obtained from **2c** (0.23 g, 1 mmol) similarly to compound **6a**. The yield was 0.22 g (60%), m.p. 245—247 °C. ^{1}H NMR, δ: 6.75 (m, 1 H, Ar); 6.9 (m, 1 H, Ar); 7.2—7.35 (m, 6 H, Ar); 7.9 (m, 1 H, Py); 8.45 (m, 1 H, Py); 8.9 (m, 1 H, Py); 9.8 (s, 1 H, NH); 10.25 (s, 1 H, NH). MS, m/z: 359$[M]^+$. Found (%): C, 63.41; H, 3.54; N, 19.60. $C_{19}H_{13}N_5O_3$. Calculated (%): C, 63.51; H, 3.65; N, 19.49.

***S*-Methyl 2-(2-nitrophenylamino)-2-oxothioacetate (7a).** Freshly distilled dimethyl sulfate (0.2 g, 1.5 mmol) was added to compound **4a** (0.26 g, 1 mmol). The mixture was heated for 40 min at 100 °C, then, cooled to room temperature followed by addition of water (2 mL). A precipitate formed was filtered off, washed with cold water and recrystallized from ethanol to obtain product **7a** (0.18 g, 87%), m.p. 132—135 °C. ^{1}H NMR, δ: 2.4 (s, 3 H, CH_3); 7.48 (m, 1 H, Ar); 7.82 (m, 1 H, Ar); 8.15 (m, 2 H, Ar); 11.25 (s, 1 H, NH). MS, m/z: 240 $[M]^+$. Found (%): C, 45.16; H, 3.25; N, 11.60; S, 13.30. $C_9H_8N_2O_4S$. Calculated (%): C, 45.00; H, 3.36; N, 11.66; S, 13.35.

***S*-Methyl 2-(4-chloro-2-nitrophenylamino)-2-oxothioacetate (7b)** was obtained from **4b** (0.33 g, 1 mmol) similarly to compound **7a**, the yield was 0.23 g (85%), m.p. 129—131 °C. ^{1}H NMR, δ: 2.4 (s, 3 H, CH_3); 7.95 (d, 1 H, Ar, J = 8.69 Hz); 8.0 (t, 1 H, Ar, J = 8.77 Hz); 8.2 (s, 1 H, Ar); 11.3 (s, 1 H, NH). MS, m/z: 274 $[M]^+$. Found (%): C, 39.15; H, 2.68; N, 10.12; S, 11.78; Cl, 13.12. $C_9H_7ClN_2O_4S$. Calculated (%): C, 39.35; H, 2.57; N, 10.20; S, 11.67; Cl, 12.91.

***S*-Methyl 2-(4-methyl-2-nitrophenylamino)-2-oxothioacetate (7c)** was obtained from **4c** (0.31 g, 1 mmol) similarly to compound **7a**, the yield was 0.22 g (87%), m.p. 187—189 °C. ^{1}H NMR, δ: 2.45 (s, 6 H, CH_3); 7.6 (d, 1 H, Ar, J = 7.92 Hz); 7.95 (t, 2 H, Ar, J = 7.11 Hz); 11.2 (s, 1 H, NH). MS, m/z: 254 $[M]^+$. Found (%): C, 47.12; H, 4.06; N, 11.06; S, 12.69. $C_{10}H_{10}N_2O_4S$. Calculated (%): C, 47.24; H, 3.96; N, 11.02; S, 12.61.

***N*-Phenyl-1*H*-benzoimidazole-2-carboxamide (8a).** Compound $SnCl_2 \cdot 2H_2O$ (1.2 g, 5 mmol) was added to monothiooxamide **3a** (0.3 g, 1 mmol). The mixture was refluxed in ethanol (7 mL) for 1 h, then cooled to room temperature, and the solvent was evaporated *in vacuo*. Water (5 mL) and 15% aq. NaOH were added to the residue. The mixture obtained was extracted with ethyl acetate; the solvent was evaporated, the residue was purified by preparative TLC (silica gel, eluent: ethyl acetate—light petroleum 1 : 3) to obtain compound **8a** (0.14 g, 58%), m.p. 234—235 °C (agrees with the data in Ref. 7).

^{1}H NMR, δ: 7.10 (m, 1 H, Ar); 7.20 (m, 3 H, Ar); 7.3 (m, 2 H, Ar); 7.55 (m, 1 H, Ar); 8.15 (d, 2 H, Ar, J = 7.96 Hz); 10.8 (s, 1 H, NH); 12.4 (s, 1 H, NH). MS, m/z: 237 $[M]^+$. Found (%): C, 70.9; H, 4.61; N, 17.80. $C_{14}H_{11}N_3O$. Calculated (%): C, 70.87; H, 4.67; N, 17.71.

***N*-Phenyl-6-methyl-1*H*-benzimidazole-2-carboxamide (8c)** was obtained from **3c** (0.32 g, 1 mmol) similarly to compound **8a**, the yield was 0.14 g (55%), m.p. 137—139 °C. ^{1}H NMR, δ: 2.4 (s, 3 H, CH_3); 6.5 (m, 1 H, Ar); 7.2 (m, 2 H, Ar); 7.3 (m, 2 H, Ar); 7.5 (m, 1 H, Ar); 7.65 (m, 2 H, Ar); 9.4 (s, 1 H, NH); 10.6 (s, 1 H, NH). MS, m/z: 251$[M]^+$. Found (%): C, 71.57; H, 5.33; N, 16.80. $C_{15}H_{13}N_3O$. Calculated (%): C, 71.70; H, 5.21; N, 16.72.

1*H*-Benzimidazole-2-carboxmorpholide (9a) was obtained from **4a** (0.3 g, 1 mmol) similarly to compound **8a**, the yield was 0.14 g (60%), m.p. 129—131 °C. ^{1}H NMR, δ: 3.1 (m, 2 H, CH_2); 3.7 (m, 2 H, CH_2); 3.85 (m, 2 H, CH_2); 4.05 (m, 2 H, CH_2); 7.2 (m, 2 H, Ar); 7.8 (m, 2 H, Ar); 11.2 (s, 1 H, NH). MS, m/z: 231 $[M]^+$. Found (%): C, 62.26; H, 5.80; N, 18.08. $C_{12}H_{13}N_3O_2$. Calculated (%): C, 62.33; H, 5.67; N, 18.17.

6-Chloro-1*H*-benzimidazole-2-carboxmorpholide (9b) was obtained from **4b** (0.33 g, 1 mmol) similarly to compound **8a**, the yield was 0.15 g (57%), m.p. 135—137 °C. ^{1}H NMR, δ: 3.05 (m, 2 H, CH_2); 3.58 (m, 2 H, CH_2); 3.75 (m, 2 H, CH_2); 4.0 (m, 2 H, CH_2); 7.25 (m, 1 H, Ar); 7.6 (m, 1 H, Ar); 7.86 (m, 1 H, Ar); 10.8 (s, 1 H, NH). MS, m/z: 265 $[M]^+$. Found (%): C, 54,45; H, 4.44; N, 15.96; Cl, 13,26. $C_{12}H_{12}ClN_3O_2$. Calculated (%): C, 54.25; H, 4.55; N, 15.82; Cl, 13.34.

6-Methyl-1*H*-benzimidazole-2-carboxmorpholide (9c) was obtained from **4c** (0.31 g, 1 mmol) similarly to compound **8a**, the yield was 0.15 g (60%), m.p. 176—179 °C. ^{1}H NMR, δ: 2.4 (s, 3 H, CH_3); 3.1 (m, 2 H, CH_2); 3.56 (m, 2 H, CH_2); 3.8 (m, 2 H, CH_2); 3.9 (m, 2 H, CH_2); 7.07 (m, 1 H, Ar); 7.5 (m, 1 H, Ar); 7.65 (m, 1 H, Ar); 11.3 (s, 1 H, NH). MS, m/z: 245 $[M]^+$. Found (%): C, 63.56; H, 6.27; N, 17.0. $C_{13}H_{15}N_3O_2$. Calculated (%): C, 63.66; H, 6.16; N, 17.13.

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