CYCLIZATION OF SEMICARBAZIDE DERIVATIVES OF 3-METHYL-5-THIOXO-4,5-DIHYDRO-1*H*-1,2,4-TRIAZOLE-4-ACETIC ACID

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Received November 19, 2002
Accepted February 17, 2003

By the reaction of hydrazide of 3-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazole-4-acetic acid (**1**) with isocyanates, 3-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazole-4-acetosemicarbazide derivatives **2** were obtained. Cyclization of these compounds in the presence of 2% NaOH led to the formation of 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives **3**, which was confirmed by X-ray analysis of **3b**.

Keywords: Triazolines; Triazoles; 1,2,4-Triazolin-5-one; Semicarbazides; Isocyanates; Hydrazides; Cyclizations; X-Ray diffraction.

Depending on the nature of substituents, derivatives of 4,5-dihydro-1*H*-1,2,4-triazol-5-one show different biological activities, such as antidepressant[1–4], anticonvulsant[5], analgesic[6], antiinflammatory[7,8], antitumor[9], antibacterial[10,11] and they can also be used as herbicides[12–16] or fungicides[17–21].

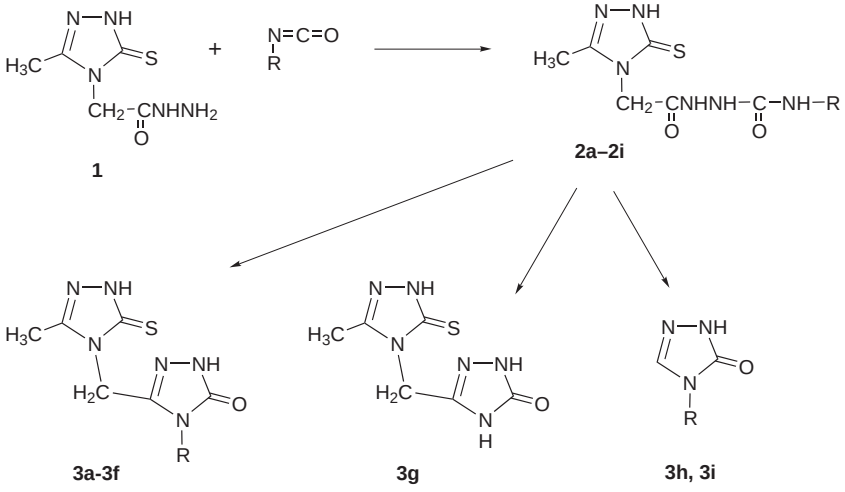
One of the methods to synthesize these compounds is cyclization of their semicarbazide derivatives in alkaline media[22–27]. The present paper is continuation of the research on chemical properties of ethyl ester of 3-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazole-4-acetic acid[28], which gave many new interesting compounds by transformation of the ester group. Here, the ethyl ester was used for preparation of hydrazide of 3-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazole-4-acetic acid[28] (**1**). Next, in the reaction of the hydrazide with isocyanates, the respective semicarbazide derivatives **2** were obtained.

Cyclization of **2a**–**2g** led to new derivatives **3a**–**3g** composed of 4,5-dihydro-1*H*-1,2,4-triazole-5-thione and 4,5-dihydro-1*H*-1,2,4-triazol-5-one systems linked through a methylene group. The cyclization of

doi:10.1135/cccc20030792

semicarbazide derivatives **2h** and **2i** led to new 4-substituted derivatives of 4,5-dihydro-1*H*-1,2,4-triazol-5-one **3h** and **3i** (Scheme 1).

Compounds **3a**–**3f** will be tested for their pharmacological activity.



2, 3	R
a	Ph
b	Et
c	n-C_6H_{11}
d	$PhCH_2$
e	4-$EtOC_6H_4$
f	$PhCHCH_3$
g	COOEt
h	PhCO
i	$PhSO_2$

SCHEME 1

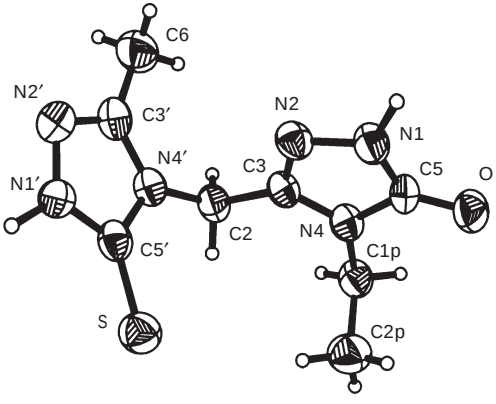
RESULTS AND DISCUSSION

New semicarbazide derivatives **2** were obtained by the reaction of the hydrazide of 3-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazole-4-acetic acid (**1**) with isocyanates. The reaction medium was anhydrous diethyl ether or *N*,*N*-dimethylacetamide and the reaction was carried out at room temperature or by heating substrates in the melt for 15 h. The conditions of the reactions were established experimentally. Semicarbazides **2** were cyclized in 2% solution of sodium hydroxide. The products of these reactions depended on the substituents in starting compounds **2**. In the case of semicarbazide derivatives with aliphatic or aromatic group **2a**–**2f**, the cyclization led to the formation of 3,4-disubstituted 4,5-dihydro-

1*H*-1,2,4-triazol-5-one ring. These compounds (**3a**–**3f**) possess aliphatic or aromatic group in position 4 of the formed ring. The structure of **3b** was confirmed by X-ray crystallography. A view of the molecule **3b** is shown in Fig. 1. All distances and angles in the rings fall within normal limits. Of two possible tautomeric forms, keto and enol, only the keto is observed in both heterocycles. The triazol-5-one and triazole-5-thione rings are planar and nearly perpendicular in the solid state; dihedral angle between their best planes is 81°.

The cyclization reaction of semicarbazide **2g**, obtained from hydrazide **1** and ethyl isocyanatoformate in alkaline medium, was accompanied by hydrolysis and decarboxylation, and finally 3-substituted 4,5-dihydro-1*H*-1,2,4-triazol-5-one **3g** was obtained.

The alkaline cyclization of semicarbazides **2h** and **2i** was quite different. During the reaction (5-thioxo-1,2,4-triazol-4-yl)methyl substituent was eliminated and 4-substituted 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives **3h** and **3i** were formed. Explanation of the character of the C–C bond splitting is under way. Structure of these two compounds was confirmed by an independent synthesis. The same compounds were also obtained by the reaction of formohydrazide with benzoyl or benzenesulfonyl isocyanate. The reaction was carried out in the melt at 115–120 °C. Mixed melting points



Bond length, Å	
N1–N2	1.368(6)
N1–C5	1.339(6)
N2–C3	1.307(7)
C3–N4	1.363(7)
N4–C5	1.384(7)
N1′–N2′	1.365(7)
N1′–C5′	1.331(8)
N2′–C3′	1.310(8)
C3′–N4′	1.369(8)
N4′–C5′	1.377(7)

FIG. 1
Perspective view of **3b** with atom numbering scheme and displacement ellipsoids at the 50% probability level

have not shown any depression. The IR and ^{1}H NMR spectra of these compounds were also identical.

Regarding the enol–keto tautomerism, we have established that all cyclization products **3a**–**3i**, exist in the keto form, both in the solid state and in solution.

EXPERIMENTAL

Melting points were determined in a Fisher–Johns block and are not corrected. IR spectra (ν, cm^{-1}) were recorded in KBr using a Specord IR-75 spectrophotometer. ^{1}H NMR spectra were recorded on a Tesla BS-567 A spectrometer (100 MHz) in DMSO-d_6 with TMS as internal standard and are given in ppm (δ-scale), *J* in Hz. The mass spectra were taken with an AMD-604 mass spectrometer using a 70 eV electron beam. ^{13}C NMR spectra were recorded on a Bruker AC 200F instrument.

Chemicals were purchased from Merck Co. or Fluka Ltd. and used without further purification. The purity of the prepared compounds was checked by TLC on Aluminium oxide 60 F_{254} plates (Merck) in a $CHCl_3/C_2H_5OH$ (10:1 and 10:2) with UV or iodine visualization. 3-Methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazole-4-acetohydrazide (**1**) was obtained in the reaction of ethyl 3-methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazole-4-acetate with 100% hydrazine hydrate[28].

Semicarbazide Derivatives of 3-Methyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazole-4-acetic Acid (**2**)

1-[(3-Methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]-4-phenylsemicarbazide (**2a**). A mixture of hydrazide **1** (1.9 g, 10 mmol) and phenyl isocyanate (1.2 g, 10 mmol) was heated at the 70–90 °C for 15 h. The product was washed with diethyl ether to remove the unreacted isocyanate and then with water to remove hydrazide residues, dried and crystallized from ethanol. Yield 2.45 g (80%), m.p. 208–210 °C. For $C_{12}H_{14}N_6O_2S$ (306.3) calculated: 47.04% C, 4.06% H, 27.40% N; found: 47.30% C, 4.39% H, 27.28% N. IR (KBr): 3317 (NH), 3064 (CH_{ar}), 2961, 1447 (CH_{al}), 1710 (C=O), 1556 (C=N). ^{1}H NMR (DMSO-d_6): 2.27 s, 3 H (CH_3); 4.87 s, 2 H (CH_2); 7.33–7.42 m, 5 H (5 × CH_{ar}); 8.24, 8.67, 10.20 3 s, 3 H (3 × NH); 13.52 s, 1 H (NH).

4-Ethyl-1-[(3-methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]semicarbazide (**2b**). A mixture of hydrazide **1** (1.9 g, 10 mmol) and ethyl isocyanate (0.71 g, 10 mmol) in 10 ml of anhydrous diethyl ether was kept at room temperature for 24 h. Then the formed compound was filtered off, washed with diethyl ether and crystallized from ethanol. Yield 2.11 g (82%), m.p. 239–240 °C. For $C_8H_{14}N_6O_2S$ (258.3) calculated: 37.20% C, 5.46% H, 32.54% N; found: 37.32% C, 5.50% H, 32.41% N. IR (KBr): 3302 (NH), 2942, 1445 (CH_{al}), 1700 (C=O), 1564 (C=N). ^{1}H NMR (DMSO-d_6): 1.05 t, 3 H, *J* = 7.1 (CH_3); 2.24 s, 3 H (CH_3); 3.12 q, 2 H, *J* = 6.8 (CH_2); 4.79 s, 2 H (CH_2); 8.21, 9.32, 9.98 3 s, 3 H (3 × NH); 13.45 s, 1 H (NH).

General Procedure for **2c**–**2i**

A solution of hydrazide **1** (1.9 g, 10 mmol) and an isocyanate (10 mmol) in 10 ml of *N*,*N*-dimethylacetamide was kept at room temperature for 24 h, and then 40 ml of water was added. The precipitate was filtered off and crystallized from ethanol. In case of compounds

2g–**2i**, dimethylacetamide was distilled off under reduced pressure and the residue was crystallized from ethanol.

4-Cyclohexyl-1-[(3-methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]semicarbazide (**2c**). Yield 2.46 g (79%), m.p. 233–235 °C. For $C_{12}H_{20}N_6O_2S$ (312.4) calculated: 46.13% C, 6.45% H, 26.91% N; found: 46.10% C, 6.33% H, 27.01% N. IR (KBr): 3302 (NH), 2931, 1419 (CH_{al}), 1708 (C=O), 1536 (C=N). ^{1}H NMR (DMSO-d_6): 1.05–1.84 m, 10 H (5 × CH_2); 2.28 s, 3 H (CH_3); 5.06 s, 2 H (CH_2); 6.14 t, 1 H, *J* = 1.8 (CH); 8.10, 9.41, 10.04 3 s, 3 H (3 × NH); 13.68 s, 1 H (NH).

4-Benzyl-1-[(3-methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]semicarbazide (**2d**). Yield 2.49 g (78%), m.p. 258–260 °C. For $C_{13}H_{16}N_6O_2S$ (320.3) calculated: 48.75% C, 5.03% H, 26.22% N; found: 48.88% C, 5.50% H, 26.00% N. IR (KBr): 3321 (NH), 3031 (CH_{ar}), 2926, 1419 (CH_{al}), 1726 (C=O), 1550 (C=N). ^{1}H NMR (DMSO-d_6): 2.28 s, 3 H (CH_3); 4.27 d, 2 H, *J* = 6.1 (CH_2); 4.90 s, 2 H (CH_2); 7.25–7.37 m, 5 H (5 × CH_{ar}); 8.36, 9.83, 10.10 3 s, 3 H (3 × NH); 13.55 s, 1 H (NH).

4-(4-Ethoxyphenyl)-1-[(3-methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]semicarbazide (**2e**). Yield 2.59 g (74%), m.p. 238–240 °C. For $C_{14}H_{18}N_6O_3S$ (350.3) calculated: 48.00% C, 5.17% H, 23.98% N; found: 47.89% C, 5.00% H, 24.10% N. IR (KBr): 3297 (NH), 3071 (CH_{ar}), 2934, 1417 (CH_{al}), 1719 (C=O), 1560 (C=N), 1247 (C–O–C). ^{1}H NMR (DMSO-d_6): 1.29 t, 3 H, *J* = 6.9 (CH_3); 2.27 s, 3 H (CH_3); 3.95 q, 2 H, *J* = 7.0 (CH_2); 4.87 s, 2 H (CH_2); 6.79–7.86 m, 4 H (4 × CH_{ar}); 8.58, 9.46, 10.18 3 s, 3 H (3 × NH); 13.55 s, 1 H (NH).

1-[(3-Methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]-4-(1-phenylethyl)semicarbazide (**2f**). Yield 2.37 g (71%), m.p. 253–255 °C. For $C_{14}H_{18}N_6O_2S$ (334.4) calculated: 50.28% C, 5.42% H, 25.13% N; found: 50.00% C, 5.21% H, 25.07% N. IR (KBr): 3267 (NH), 3070 (CH_{ar}), 2928, 1426 (CH_{al}), 1703 (C=O), 1579 (C=N). ^{1}H NMR (DMSO-d_6): 1.34 d, 3 H, *J* = 7.0 (CH_3); 2.27 s, 3 H (CH_3); 4.85 s, 2 H (CH_2); 6.67 q, 1 H, *J* = 7.5 (CH); 7.17–7.93 m, 5 H (5 × CH_{ar}); 8.31, 9.35, 10.04 3 s, 3 H (3 × NH); 13.52 s, 1 H (NH).

4-Ethoxycarbonyl-1-[(3-methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]semicarbazide (**2g**). Yield 1.96 g (65%), m.p. 220–221 °C. For $C_9H_{14}N_6O_4S$ (302.2) calculated: 35.76% C, 4.66% H, 27.79% N; found: 35.58% C, 4.70% H, 27.81% N. IR (KBr): 3307(NH), 2967, 1422 (CH_{al}), 1720 ($C{=}O_{estr}$), 1686 (C=O), 1583 (C=N). ^{1}H NMR (DMSO-d_6): 1.21 t, 3 H, *J* = 7.1 (CH_3); 2.24 s, 3 H (CH_3); 4.13 q, 2 H, *J* = 7.1 (CH_2); 4.78 s, 2 H (CH_2); 9.28, 10.32, 10.44 3 s, 3 H (3 × NH); 13.51 s, 1 H (NH).

4-Benzoyl-1-[(3-methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]semicarbazide (**2h**). Yield 2.37 g (71%), m.p. 266–268 °C. For $C_{13}H_{14}N_6O_3S$ (334.2) calculated: 46.71% C, 4.22% H, 25.13% N; found: 46.58% C, 4.11% H, 25.02% N. IR (KBr): 3239 (NH), 3068 (CH_{ar}), 2960, 1418 (CH_{al}), 1711 (C=O), 1671 (C=O), 1583 (C=N). ^{1}H NMR (DMSO-d_6): 2.28 s, 3 H (CH_3); 4.91 s, 2 H (CH_2); 7.51–8.02 m, 5 H (5 × CH_{ar}); 10.15, 10.67, 11.06 3 s, 3 H (3 × NH); 13.54 s, 1 H (NH).

4-(Benzenesulfonyl)-1-[(3-methyl-5-thioxo-3,4-dihydro-1H-1,2,4-triazol-4-yl)acetyl]semicarbazide (**2i**). Yield 2.51 g (68%), m.p. 188–190 °C. For $C_{12}H_{14}N_6O_4S_2$ (370.2) calculated: 38.92% C, 3.81% H, 22.68% N; found: 38.76% C, 3.74% H, 22.90% N. IR (KBr): 3310 (NH), 3054 (CH_{ar}), 2949, 1419 (CH_{al}), 1716 (C=O), 1585 (C=N), 1350, 1160 (S=O). ^{1}H NMR (DMSO-d_6): 2.24 s, 3 H (CH_3); 4.79 s, 2 H (CH_2); 7.36–7.88 m, 5 H (5 × CH_{ar}); 9.79, 9.92, 10.28 3 s, 3 H (3 × NH); 13.52 s, 1 H (NH).

3,4-Disubstituted 4,5-Dihydro-1*H*-1,2,4-triazol-5-ones **3a**–**3f**, 3-Substituted 4,5-Dihydro-1*H*-1,2,4-triazol-5-one **3g** and 4-Substituted 1*H*-1,2,4-Triazol-5-ones **3h**, **3i**

Method A for **3a**–**3i**

A mixture of semicarbazide **2a**–**2i** (10 mmol) and 40–50 ml of 2% solution of sodium hydroxide was boiled for 15–20 h (40 h for **2f**, 2 h for **2g** and 5 h for **2h**, **2i**). After cooling, the solution was neutralized with dilute hydrochloric acid. The precipitate was filtered off and then crystallized from ethanol.

Method B for **3h** *and* **3i**

A mixture of formohydrazide (0.6 g, 10 mmol) and benzoyl or benzenesulfonyl isocyanate (10 mmol) was heated at 115–120 °C for 20 h. The product was washed with diethyl ether to remove the unreacted isocyanate, dried and crystallized from ethanol.

3-[(3-Methyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)methyl]-4-phenyl-4,5-dihydro-1H-1,2,4-triazol-5-one (**3a**). Yield 1.73 g (60%), m.p. 308–310 °C. For $C_{12}H_{12}N_6OS$ (288.3) calculated: 49.97% C, 4.19% H, 29.15% N; found: 50.03% C, 3.94% H, 29.39% N. IR (KBr): 3074 (CH_{ar}), 2950, 1421 (CH_{al}), 1718 (C=O), 1589 (C=N), 1505 (C–N). ^{1}H NMR (DMSO-d_6): 2.30 s, 3 H (CH_3); 5.03 s, 2 H (CH_2); 7.48–7.58 m, 5 H (5 × CH_{ar}); 11.91 s, 1 H (NH); 13.54 s, 1 H (NH).

4-Ethyl-3-[(3-methyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)methyl]-4,5-dihydro-1H-1,2,4-triazol-5-one (**3b**). Yield 1.68 g (70%), m.p. 284–286 °C. For $C_8H_{12}N_6OS$ (240.3) calculated: 39.97% C, 5.03% H, 34.98% N; found: 39.62% C, 5.28% H, 34.55% N. IR (KBr): 2966, 1420 (CH_{al}), 1723 (C=O), 1581 (C=N), 1507 (C–N). ^{1}H NMR (DMSO-d_6): 1.12 t, 3 H, J = 7.1 (CH_3); 2.30 s, 3 H (CH_3); 2.73 q, 2 H, J = 6.9 (CH_2); 5.23 s, 2 H (CH_2); 11.71 s, 1 H (NH); 13.66 s, 1 H (NH). ^{13}C NMR: 11.21 (CH_3); 14.29 (CH_3); 35.57 (CH_2); 39.92 (CH_2); 142.06, 149.99 (2 × C_{ar}); 154.73 (C=O); 166.01 (C=S). MS, *m/z* (%): 240 (M^+, 86), 211 (4), 208 (27), 154 (7), 128 (25), 114 (100), 100 (13), 56 (41), 41 (14).

X-Ray analysis. Diffraction data were measured at 295 K on a KM4 diffractometer using variable scan speed (ω–2θ scan mode) and graphite-monochromatized CuKα radiation (λ = 1.54178 Å). A single crystal of dimensions 0.7 × 0.08 × 0.04 mm was used. The crystal is triclinic, space group $P\bar{1}$, a = 4.659(1) Å, b = 10.029(2) Å, c = 12.361(2) Å, α = 87.28(3)°, β = 82.69(3)°, γ = 77.76(3)°, V = 559.7 (2) Å^3, Z = 2, d_{calc} = 1.426 g cm^{-3}, μ = 2.525 mm^{-1}. Reflections were collected up to θ_{max} = 80.2°; of 2711 measured reflections, 2420 were independent (R_{int} = 0.1039) and were used in the calculations. Crystal structure was solved by direct methods using the SHELXS97 [29] program and refined by the full-matrix least-squares on F^2 using the SHELXL97 [30]. The non-hydrogen atoms were refined with anisotropic displacement parameters. H-atom positions were located from the geometry, and isotropic factors of 1.2 U_{eq} of the bonded C-atoms are given; the C–H bond riding model was used in the refinement. Final discrepancy factors are R_1 = 0.0889, wR_2 = 0.1453 for $I > 2\sigma(I)$, and S = 0.968. CCDC 196 638 contains the supplementary crystallographic data for compound **3b**. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

4-Cyclohexyl-3-[(3-methyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)methyl]-4,5-dihydro-1H-1,2,4-triazol-5-one (**3c**). Yield 1.79 g (61%), m.p. 244–246 °C. For $C_{12}H_{18}N_6OS$ (294.4) calculated: 48.96% C, 6.16% H, 28.56% N; found: 48.68% C, 6.06% H, 28.62% N. IR (KBr): 3062 (CH_{ar}), 2945, 1431 (CH_{al}), 1710 (C=O), 1580 (C=N), 1530 (C–N). ^{1}H NMR (DMSO-d_6): 1.05–2.13 m, 10 H (5 × CH_2); 2.25 s, 3 H (CH_3); 4.13 t, 1 H, J = 2.0 (CH); 5.24 s, 2 H (CH_2); 11.63 s, 1 H (NH); 13.66 s, 1 H (NH).

4-Benzyl-3-[(3-methyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)methyl]-4,5-dihydro-1H-1,2,4-triazol-5-one (**3d**). Yield 1.87 g (62%), m.p. 248–250 °C. For $C_{13}H_{14}N_6OS$ (302.2) calculated: 51.65% C, 4.66% H, 27.79% N; found: 51.78% C, 4.55% H, 28.00% N. IR (KBr): 3065 (CH_{ar}), 2961, 1430 (CH_{al}), 1694 (C=O), 1587 (C=N), 1510 (C–N). ^{1}H NMR (DMSO-d_6): 2.18 s, 3 H (CH_3); 4.97 s, 2 H (CH_2); 5.14 s, 2 H (CH_2); 7.29–7.37 m, 5 H (5 × CH_{ar}); 11.88 s, 1 H (NH); 13.52 s, 1 H (NH). ^{13}C NMR: 11.07 (CH_3); 40.33 (CH_2); 43.41 (CH_2); 126.47, 127.54, 128.59, 136.12 (6 × CH_{ar}); 142.25, 149.60 (2 × C_{ar}); 155.04 (C=O); 166.63 (C=S). MS, *m/z* (%): 302 (M^+, 84), 270 (100), 211 (5), 188 (21), 154 (12), 114 (17), 91 (73), 77 (4).

4-(4-Ethoxyphenyl)-3-[(3-methyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)methyl]-4,5-dihydro-1H-1,2,4-triazol-5-one (**3e**). Yield 2.19 g (66%), m.p. 256–258 °C. For $C_{14}H_{16}N_6O_2S$ (332.3) calculated: 50.60% C, 4.85% H, 25.28% N; found: 51.05% C, 5.00% H, 25.15% N. IR (KBr): 3070 (CH_{ar}), 2974, 1443 (CH_{al}), 1698 (C=O), 1589 (C=N), 1518 (C–N), 1 262 (C–O–C). ^{1}H NMR (DMSO-d_6): 1.34 t, 3 H, J = 6.8 (CH_3); 2.47 s, 3 H (CH_3); 4.08 q, 2 H, J = 6.9 (CH_2); 4.99 s, 2 H (CH_2); 7.03–7.45 m, 4 H (4 × CH_{ar}); 11.85 s, 1 H (NH); 13.54 s, 1 H (NH).

3-[(3-Methyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)methyl]-4-(1-phenylethyl)-4,5-dihydro-1H-1,2,4-triazol-5-one (**3f**). Yield 2.05 g (65%), m.p. 132–134 °C. For $C_{14}H_{16}N_6OS$ (316.4) calculated: 53.14% C, 5.09% H, 26.55% N; found: 53.07% C, 5.10% H, 26.77% N. IR (KBr): 3068 (CH_{ar}), 2970, 1440 (CH_{al}), 1714 (C=O), 1570 (C=N), 1528 (C–N). ^{1}H NMR (DMSO-d_6): 1.80 d, 3 H, J = 7.1 (CH_3); 2.16 s, 3 H (CH_3); 5.00 s, 2 H (CH_2); 5.54 q, 1 H, J = 7.4 (CH); 7.34–7.93 m, 5 H (5 × CH_{ar}); 11.76 s, 1 H (NH); 13.55 s, 1 H (NH).

3-[(3-Methyl-5-thioxo-4,5-dihydro-1H-1,2,4-triazol-4-yl)methyl]-4,5-dihydro-1H-1,2,4-triazol-5-one (**3g**). Yield 1.44 g (68%), m.p. 195–197 °C. For $C_6H_8N_6OS$ (212.1) calculated: 33.97% C, 3.80% H, 39.59% N; found: 33.85% C, 3.90% H, 39.32% N. IR (KBr): 2969, 1460 (CH_{al}), 1708 (C=O), 1585 (C=N), 1490 (C–N). ^{1}H NMR (DMSO-d_6): 2.26 s, 3 H (CH_3); 4.78 s, 2 H (CH_2); 9.80 s, 1 H (NH); 13.52 s, 1 H (NH).

4-Benzoyl-4,5-dihydro-1H-1,2,4-triazol-5-one (**3h**). Yield 1.04 g (55%) (method *A*) and 1.0 g (53%) (method *B*), m.p. 115–117 °C. For $C_9H_7N_3O_2$ (189.2) calculated: 75.14% C, 3.70% H, 22.22% N; found: 75.07% C, 3.68% H, 22.37% N. IR (KBr): 3071 (CH_{ar}), 1688 (C=O), 1582 (C=N), 1547 (C–N). ^{1}H NMR (DMSO-d_6): 7.41 s, 1 H (CH); 7.44–8.02 m, 5 H (5 × CH_{ar}); 12.70 s, 1 H (NH).

4-(Benzenesulfonyl)-4,5-dihydro-1H-1,2,4-triazol-5-one (**3i**). Yield 1.33 g (53%) (method *A*) and 1.30 g (52%) (method *B*), m.p. 151 °C. For $C_8H_7N_3O_3S$ (225.1) calculated: 42.67% C, 3.13% H, 18.65% N; found: 42.78% C, 3.45% H, 18.77% N. IR (KBr): 3041 (CH_{ar}), 1708 (C=O), 1512 (C=N), 1454 (C–N), 1 354, 1 172 (S=O). ^{1}H NMR (DMSO-d_6): 7.44 s, 1 H (CH); 7.50–8.02 m, 5 H (5 × CH_{ar}); 10.54 s, 1 H (NH).

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