On Triazoles. XXXIII [1]. The Reaction of Potassium Triazolyldithiocarbonates with Dihaloalkanes [2]

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Received February 26, 1993

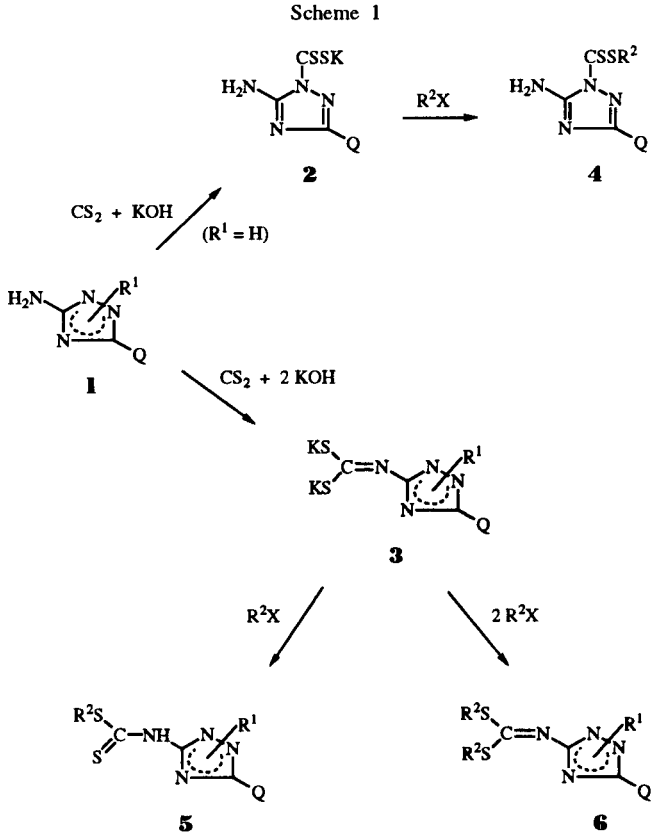
The reaction of potassium (5-amino-3-Q-1,2,4-triazolyl)dithiocarbonates **2** with 1,ω-dihaloalkanes **7-10** to yield ω-haloalkyldithiocarbonates **11-12**, 1,ω-alkylene-bis(dithiocarbonates) **13-15** and different by-products as the corresponding 7,8-dihydro[1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazepine-5(9*H*)-thione (**16**), 7,8,9,10-tetrahydro[1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazocine-5-thione (**17**) and 1,7-dihydro-5*H*-1,2,4-triazolo[1,5-*c*][1,3,5]thiadiazine-5-thione (**22**) derivatives all three representing novel ring systems were obtained. Repeating the reactions with dipotassium salts **3** the corresponding iminodithietans **18**, imino-1,3-dithiolanes **19** and imino-1,3-dithianes **20** were obtained. Unexpectively, the imino-1,3-dithiolanes (**19**) rearranged to the corresponding thiazolidines **24-27** under rather mild conditions. A possible mechanism is proposed for this rearrangement.

J. Heterocyclic Chem., **31**, 997 (1994).

In the previous papers of this series [3,4] we have studied the alkylation of the potassium salts of different 1,2,4-triazolyldithiocarbonates **2-3** prepared from the corresponding 5-amino-3-Q-1,2,4-triazole derivatives **1**, to yield type **4** alkyl, aralkyl and aryl (5-amino-3-Q-1,2,4-triazol-1-yl)dithiocarbonates, type **5** alkyl (3-Q-1,2,4-triazol-5-ylamino)dithiocarbonates and type **6** dialkyl (3-Q-1,2,4-triazol-5-ylimino)dithiocarbonates, respectively (Scheme 1).

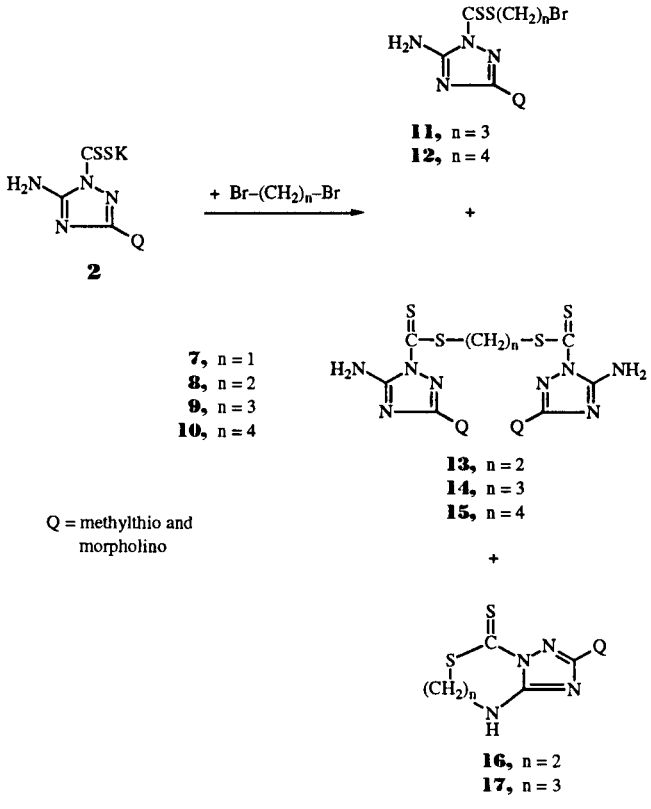
As a continuation of the above studies we will now report on the reactions of the above potassium salts with dihaloalkanes. The reaction of potassium (5-amino-3-methylthio and morpholino)-1,2,4-triazol-1-yl)dithiobarbonates **2** (Q = methylthio and morpholino, respectively) prepared "*in situ*" from the corresponding 5-amino-3-Q-1*H*-1,2,4-triazoles **1** (Q = methylthio and morpholino, respectively) with 1,3-dibromopropane (**9**) and 1,4-dibromobutane (**10**) led to the corresponding (ω-bromoalkyl) [5-amino-3-(methylthio and morpholino)-1,2,4-triazol-1-yl]dithiocarbonates **11** and **12** (Q = methylthio and morpholino, respectively), besides the corresponding alkylene bis(dithioesters) **14** and **15** (Q = methylthio and morpholino, respectively) (Scheme 2). In the case of 1,2-dibromoethane (**8**) the corresponding (2-bromoethyl) [5-amino-3-(methylthio and morpholino)-1,2,4-triazol-1-yl]dithiocarbonates detected even by tlc were not isolated from the reaction mixtures causing severe allergies. Instead only the scarcley soluble products that could be filtered off from the reaction mixtures were isolated, namely the corresponding 1,2-ethylene bis(dithioesters) **13** (Q = methylthio and morpholino, respectively) and in the case of Q = morpholino also a ring closed bicyclic derivative, the 2-morpholino-7,8-dihydro[1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazepine-5(9*H*)-thione (**16**) that represents a novel ring system. Careful checking of the mother liquors of the scarcely soluble product obtained in

Scheme 1



an analogues reaction of **2** (Q = morpholino) and 1,3-dibromopropane (**9**) helped to find and isolate the corresponding thiadiazocine analogue of **16**, namely the 2-morpholino-7,8,9,10-tetrahydro[1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazocine-5-thione (**17**), too, also representing a novel ring system.

Scheme 2

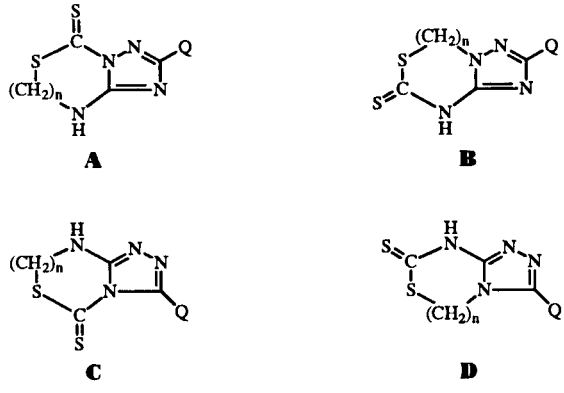


The structure of the (ω-bromoalkyl) [5-amino-3-(methylthio and morpholino)-1,2,4-triazol-1-yl]dithiocarbonates **11** and **12** (Q = methylthio and morpholino, respectively), was easily proved on the basis of the analogy of their pmr and cmr spectra taken in DMSO-d_6 solution with those of different (5-amino-3-Q-triazol-1-yl)dithiocarbonates **4** [3] [compare *e.g.* δ NH_2 of **12-13** = 8.65-8.68 ppm with **4** [3], δ NH_2 = 7.7-8.7 ppm, or δ C-3, δ C-5 and δ C=S of **12-13** = 161.8-162.7 ppm, 157.3-157.5 ppm, and 193.6-196.6 ppm, respectively, with **4** [3], δ C-3, δ C-5 and δ C=S = 161.1-164.4 ppm, 157.1-159.2 ppm, and 189.2-199.7 ppm, respectively].

The situation was the same with the corresponding alkylenebis(dithioesters) **13, 14** and **15** (Q = methylthio and morpholino, respectively) posessing again owing to their doubled (5-amino-3-Q-triazol-1-yl)dithiocarbonate structure very similar pmr and cmr spectra [see *e.g.* their δ NH_2 = 8.60-8.68 ppm, or δ C-3, δ C-5 and δ C=S = 157.5-157.6 ppm, 162.1-163.2 ppm, and 193.1-195.8 ppm data, respectively].

On the other hand, the structure of the [1,2,4]triazolo-[1,5-*c*][1,3,5]thiadiazepine (**16**, n = 2) and the corresponding [1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazocine (**17**, n = 3) derivatives had to be proved. Their condensed ring structure was in accordance with the stable molecular ions observed in the mass spectra. However, in the reactions of **2** (Q = morpholino) and the corresponding 1,2 and 1,3-dibromoalkanes, **8** and **9**, respectively any of the ring systems **A-D** (Scheme 3) arising from the possible isomerisation of the dithioester moiety [3] and different possibilities of the ring closure could be formed.

Scheme 3

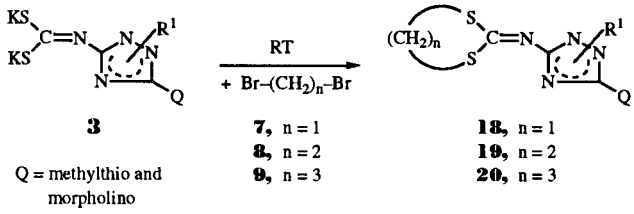


The cmr spectra helped us to make a decision among structures **A-D**, as the chemical shifts of the carbon atoms of the triazole rings were completely analogous to those of derivatives **4** [compare *e.g.* **4** (Q = morpholino, R^2 = methyl) [3], δ C-3 = 164.2 and δ C-5 = 158.8 with the analogues δ C-2 = 163.5 and 163.6, and δ C-9a or δ C-10a = 158.9 and 158.9, respectively, for **16** (Q = morpholino, n = 2) and **17** (Q = morpholino, n = 3), respectively] proving unequivocally the type **A** structure for derivatives **16** and **17** shown on Scheme 2.

Reacting the dipotassium salts **3** formed *in situ* from the corresponding derivatives **1**, carbon disulfide and excess of potassium hydroxide with dibromomethane **7**, 1,2-dibromoethane **8** and 1,3-dibromopropane **9** the corresponding imino-1,3-dithietanes **18**, imino-1,3-dithiolanes **19** and imino-1,3-dithianes **20** were obtained (Scheme 4). Their structure was again in accordance with the pmr and cmr spectra recorded. Thus the substituted triazole moieties appeared with the chemical shifts expected (see Experimental) and the methylene protons and that of carbon atoms of the newly built in rings appeared as a conse-

quence of the symmetricity in the case of derivatives **18** and **19** collapsed into one signal and in case of **20** into two signals.

Scheme 4



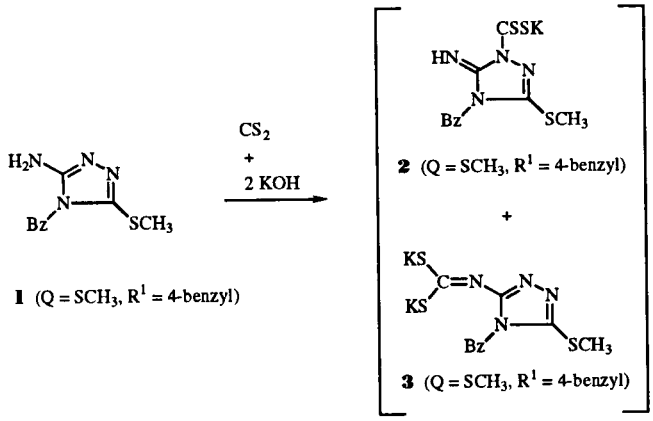
3 Q = methylthio and morpholino

7, n = 1; **8**, n = 2; **9**, n = 3

18, n = 1; **19**, n = 2; **20**, n = 3

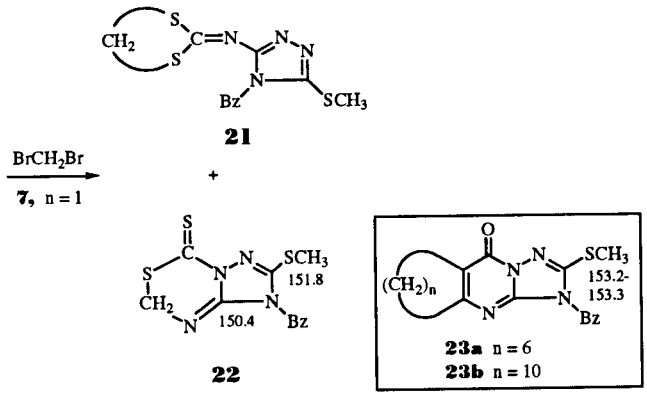
In the reaction of **3** (Q = methylthio, R^1 = 4-benzyl) prepared *in situ* from **1** (Q = methylthio, R^1 = 4-benzyl), carbon disulfide and potassium hydroxide with dibromomethane (**7**) besides the expected dithietane **21** (Q = methylthio) a by-product **22** could also be isolated that proved to be 1-benzyl-1,7-dihydro-2-methylthio-1,2,4-triazolo[1,5-*c*][1,3,5]thiadiazine-5-thione also representing a novel ring system (Scheme 5).

Scheme 5



1 (Q = SCH_3, R^1 = 4-benzyl)

2 (Q = SCH_3, R^1 = 4-benzyl) + **3** (Q = SCH_3, R^1 = 4-benzyl)



21

22

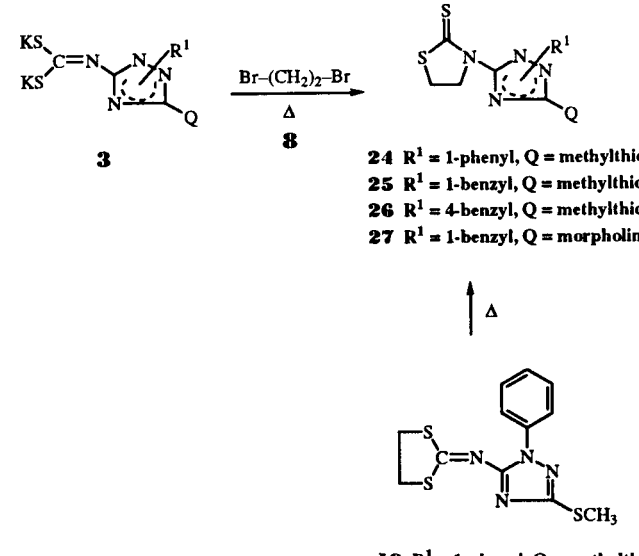
23a n = 6; **23b** n = 10

Its condensed ring structure proposed on the basis of the relatively stable molecular ion in the mass spectra corroborates also the pmr and cmr spectra recorded where the newly built in methylene group 7 appeared with the chemical shifts of 5.35 ppm and 47.5 ppm, respectively, along with the chemical shifts of the triazole carbon atoms (δ C-2 = 151.8 ppm, δ C-8a = 150.4 ppm) that were despite of the lack of a double bound in the 1,3,5-thiadiazine ring analogues to those of the known [8] 1-benzyl-6,7,8,9,10,11-hexahydro-2-methylthiocycloocta[*d*][1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (**23a**) and 1-benzyl-6,7,8,9,10,11,12,13,14,15-decahydro-2-methylthiocyclododeca[*d*]-[1,2,4]triazolo[1,5-*a*]pyrimidin-5(1*H*)-one (**23b**) (Scheme 5) appearing at 153.2-153.3 ppm, and 147.2-147.7 ppm, respectively. The thiocarbonyl carbon atom appearing at 196.5 ppm is also in accordance with the structure **22** proposed being analogues with that of derivatives **4** (see above).

Providing the reaction of the dipotassium salts **3** with 1,2-dibromoethane (**8**) at higher temperature (50°) instead of the corresponding iminodithiolanes **19** thiazolidine-2-thione derivatives **24-27** were obtained characterised by the two well separated NCH_2 and SCH_2 signals in the pmr and cmr as well as the C=S signals appearing between 180.5-183.8 ppm (see Experimental), most probably formed by thermal rearrangement of the corresponding dithiolanes. This thermal rearrangement was proved by simple recrystallisation of **19** (R^1 = phenyl, Q = methylthio) from boiling ethanol to yield **24** (R^1 = phenyl, Q = methylthio).

A similar thermal rearrangement of 2-methyl- and 2-ethyliminodithiolanes to the corresponding thiazolidine-2-thiones was observed by Ueno and coworkers [5]. However, their derivatives rearranged at only 200°, moreover the corresponding 2-phenylimino-1,3-dithiolane did not rearrange even under more severe conditions. The authors proposed a "concerted" SN_2 mechanism through the intermediate **28** (Scheme 7) for the above rearrangements.

Scheme 6

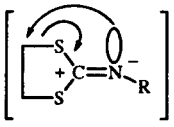


3

24 R^1 = 1-phenyl, Q = methylthio
25 R^1 = 1-benzyl, Q = methylthio
26 R^1 = 4-benzyl, Q = methylthio
27 R^1 = 1-benzyl, Q = morpholino

19 R^1 = 1-phenyl, Q = methylthio

Scheme 7



28

Scheme 8

19 **29**

Surprisingly, our 2-(1-phenyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithiolane (**19**, R^1 = phenyl, Q = methylthio) rearranged just in boiling ethanol, moreover those of 1-benzyl-3-methylthio-, 4-benzyl-3-methylthio- and 1-benzyl-3-morpholino derivatives **19** even providing the reactions at room temperature rearranged spontaneously to the corresponding thiazolidine derivatives **25**, **26** and **27**, respectively, making impossible their isolation. This easy rearrangement may be due to a different reaction mechanism. Most probably our reaction starts by the cleavage of the C-S bond of the dithiolane ring enhanced by its increased polarisation caused by the triazole nitrogen atoms to yield "ion pair" **29** as an intermediate (Scheme 8) that is stabilised by an intramolecular ring closure to yield thiazolidines **24-27**.

EXPERIMENTAL

Melting points were determined on a Koffler-Boëtius micro apparatus and are uncorrected. The infrared spectra were obtained as potassium bromide pellets using a Perkin-Elmer 577 spectrophotometer. The ultraviolet spectra were obtained with Varian Cary 118 and Pye Unicam SP 8-150 instruments. The ^{1}H-nmr and the ^{13}C-nmr measurements were performed using Varian XL-100, Bruker WM-250 and Bruker WP-80 SY instruments.

Warning! All reaction mixtures leading to ω-halolakyldithioesters caused severe allergic symptoms!

1,2-Ethylene-bis (5-Amino-3-methylthio-1*H*-1,2,4-triazol-1-yl)dithiocarbonate (**13**, Q = methylthio).

To a solution of 5.30 g (0.04 mole) of 5-amino-3-methylthio-1*H*-1,2,4-triazole (**1**, Q = methylthio, R^1 = H) [6] in a mixture of 25 ml of dimethylformamide and 15 ml of water 2.52 ml (3.2 g, 0.042 mole) of carbon disulfide, a solution of 2.6 g (0.046 mole) of potassium hydroxide in 10 ml of water and 3.45 ml (7.5 g, 0.04 mole) of 1,2-dibromoethane (**8**), respectively, were added dropwise with stirring below 10°. After standing overnight at room temperature 200 ml of water was added to the reaction mixture, the product was extracted twice with 150 ml portions of chloroform, the combined chloroform layers were washed with water, dried over anhydrous sodium sulfate and evaporated to dryness to yield 7.0 g of a honey-like material which after short refluxing with 40 ml of 2-propanol crystallised to yield 0.5 g (6%) of 1,2-ethylene-bis (5-amino-3-methylthio-1*H*-1,2,4-triazol-1-yl)dithiocarbonate (**13**, Q = methylthio) that after recrystallisation from dimethylformamide melted at 253-255°; ir: ν NH_2 = 3340 and 3200 cm^{-1}, ν C=N = 1649 and 1645 cm^{-1}, ν C=S = 1275 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.50 (s, 6H, SCH_3), 3.57 (s, 4H, SCH_2), 8.6 (bs, 4H, NH_2); cmr (DMSO-d_6): δ ppm 13.0 (SCH_3), 32.8 (SCH_2), 157.6 (C-5), 163.2 (C-3), 195.8 (C=S).

Anal. Calcd. for $C_{10}H_{14}N_8S_6$ (MW 438.66): C, 27.38; H, 3.22; N, 25.54; S, 43.86. Found: C, 27.31; H, 3.32; N, 25.60; S, 43.65.

1,2-Ethylene-bis (5-Amino-3-morpholino-1*H*-1,2,4-triazole-1-yl)dithiocarbonate (**13**, Q = morpholino) and 2-Morpholino-7,8-dihydro[1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazepine-5(9*H*)-thione (**16**, Q = morpholino).

To a solution of 6.76 g (0.04 mole) of 5-amino-3-morpholino-1*H*-1,2,4-triazole (**1a**) [7] in a mixture of 25 ml of dimethylformamide and 15 ml of water 2.52 ml (3.2 g, 0.042 mole) of carbon disulfide, a solution of 2.6 g (0.046 mole) of potassium hydroxide in 10 ml of water and 3.45 ml (7.5 g, 0.04 mole) of 1,2-dibromo-ethane (**8**), respectively, were added dropwise with stirring below 10°. After standing overnight at room temperature 200 ml of water was added to the reaction mixture, the product that precipitated was filtered off to yield 5.4 g of a crystalline material that melted at 220-255° and proved to be the mixture of 1,2-ethylene-bis (5-amino-3-morpholino-1*H*-1,2,4-triazole-1-yl)dithiocarbonate (**13**, Q = morpholino) and 2-morpholino-7,8-dihydro-[1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazepine-5-(9*H*)-thione (**16**). After two recrystallisations from dioxane 2.0 g (19%) of pure 1,2-ethylene-bis (5-amino-3-methylthio-1*H*-1,2,4-triazole-1-yl)dithiocarbonate (**13**, Q = morpholino) was obtained that melted at 271-274°; ir: ν NH_2 = 3340 and 3200 cm^{-1}, ν C=N = 1648 and 1574 cm^{-1}, ν C=S = 1277 cm^{-1}; pmr (DMSO-d_6); δ ppm 3.37 [t (J = 4.5 Hz), 8H, NCH_2], 3.50 (bs, 4H, SCH_2), 3.65 [t (J = 4.5 Hz), 8H, OCH_2], 8.64 (bs, 4H, NH_2); cmr (DMSO-d_6): δ ppm 32.6 (SCH_2), 45.1 (NCH_2), 65.4 (OCH_2), 157.5 (C-5), 162.1 (C-3), 193.1 (C=S).

Anal. Calcd. for $C_{16}H_{24}N_{10}O_2S_4$ (MW 516.70): C, 37.19; H, 4.68; N, 27.11; S, 24.82. Found: C, 36.99; H, 4.63; N, 27.30; S, 24.80.

The combined dioxane containing mother liquors were evaporated *in vacuo* to dryness and the residue was recrystallised twice from dimethylformamide to yield 1.5 g (14%) of 2-morpholino-7,8-dihydro[1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazepine-5(9*H*)-thione (**16**, Q = morpholino), mp 218-220°; ir: ν NH = 3380 cm^{-1}, ν C=N = 1670 and 1600 cm^{-1}, ν C=S = 1280 cm^{-1}; pmr (DMSO-d_6): δ ppm 3.27 (t, 2H, SCH_2), 3.25 (t, 4H, NCH_2), 3.60 (qa, 2H, $NHCH_2$), 3.65 (t, 2H, OCH_2), 10.5 (b, 1H, NH); cmr (DMSO-d_6): δ ppm 28.5 (SCH_2), 35.6 ($NHCH_2$), 46.5 (NCH_2), 65.6 (OCH_2), 158.8 (C-9a), 163.6 (C-2), 195.8 (C=S); ms: M^+ = 271.

Anal. Calcd. for $C_9H_{13}N_5OS_2$ (MW 271.37): C, 39.84; H, 4.83; N, 25.81; S, 23.63. Found: C, 39.75; H, 4.88; N, 25.78; S, 23.69.

(3-Bromopropyl) 5-Amino-3-methylthio-1*H*-1,2,4-triazole-1-yl-dithiocarbonate (**11**, Q = methylthio, n = 3).

To a solution of 5.30 g (0.04 mole) of 5-amino-3-methylthio-1*H*-1,2,4-triazole (**1**, Q = methylthio, R^1 = H) [6] in a mixture of 25 ml of dimethylformamide and 15 ml of water 2.52 ml (3.2 g, 0.042 mole) of carbon disulfide, the solution of 2.6 g (0.046 mole) of po-

tassium hydroxide in 10 ml of water and 4.07 ml (8.04 g, 0.04 mole) of 1,3-dibromopropane (**5**), respectively, were added dropwise with stirring below 10°. After standing overnight at room temperature 200 ml of water was added to the reaction mixture, the crystals which precipitated were filtered off to yield 7.0 g (53%) of (3-bromopropyl) 5-amino-3-methylthio-1*H*-1,2,4-triazole-1-yl-dithiocarbonate (**11**, Q = methylthio, n = 3) which after two recrystallisations from acetonitrile melted at 147-153°; ir: ν NH_2 = 3340 and 3210 cm^{-1}, ν C=N = 1650 and 1490 cm^{-1}, ν C=S = 1270 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.21 [qi (J = 7 Hz), 2H, CCH_2C], 2.51 (s, 3H, SCH_3), 3.29 [t (J = 7 Hz), 2H, SCH_2], 3.63 [t (J = 7 Hz), 2H, $BrCH_2$], 8.6 (bs, 2H, NH_2); cmr (DMSO-d_6): δ ppm 30.1 (CCH_2C), 32.8 ($BrCH_2$), 33.2 (SCH_2), 157.5 (C-5), 162.2 (C-3), 196.6 (C=S), ms: M^+ = 327.

Anal. Calcd. for $C_7H_{11}BrN_4S_3$ (MW 327.30): C, 25.69; H, 3.39; N, 17.12; S, 29.39, Br, 24.41. Found: C, 25.81; H, 3.56; N, 17.06; S, 29.18.

(3-Bromopropyl) 5-Amino-3-morpholino-1*H*-1,2,4-triazole-1-yl-dithiocarbonate (**11**, Q = morpholino, n = 3), 1,3-Propylene-bis (5-Amino-3-morpholino-1*H*-1,2,4-triazol-1-yl)dithiocarbonate (**14**, Q = morpholino, n = 3) and 2-Morpholino-7,8,9,10-tetrahydro-1,2,4-triazolo[1,5-*c*][1,3,5]thiadiazocine-5-thione (**17**, Q = morpholino).

To a solution of 6.76 g (0.04 mole) of 5-amino-3-morpholino-1*H*-1,2,4-triazole (**1**, Q = morpholino, R^1 = H) [7] in a mixture of 25 ml of dimethylformamide and 15 ml of water 2.52 ml (3.2 g, 0.042 mole) of carbon disulfide, the solution of 2.6 g (0.046 mole) of potassium hydroxide in 10 ml of water and 4.07 ml (8.04 g, 0.04 mole) of 1,3-dibromopropane (**9**), respectively, were added by dropping them to the reaction mixture with stirring below 10°. After standing overnight at room temperature the crystals which precipitated were filtered off and washed with a small amount of acetionitrile to yield 9.25 g of a product that was a mixture of (3-bromopropyl) 5-amino-3-morpholino-1*H*-1,2,4-triazol-1-yl-dithiocarbonate (**11**, Q = morpholino, n = 3), 1,3-propylene-bis (5-amino-3-morpholino-1*H*-1,2,4-triazol-1-yl)dithiocarbonate (**14**, Q = morpholino, n = 3) and 2-morpholino-7,8,9,10-tetrahydro[1,2,4]triazolo[1,5-*c*][1,3,5]thiadiazocine-5-thione (**17**, Q = morpholino). This was refluxed for 2 minutes with 50 ml of acetonitrile and filtered while hot. The filtrate crystallised to yield 3.0 g (20%) of (3-bromopropyl) 5-amino-3-morpholino-1*H*-1,2,4-triazol-1-yl-dithiocarbonate (**11**, Q = morpholino, n = 3) that after further recrystallisation from acetonitrile melted at 143-146°; ir: ν NH_2 = 3340 and 3285 cm^{-1}, ν C=N = 1667 and 1578 cm^{-1}, ν C=S = 1280 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.19 [qi (J = 7 Hz), 2H, CCH_2C], 3.24 [t (J = 7 Hz), 2H, SCH_2], 3.37 [t (J = 4.5 Hz), 4H, NCH_2], 3.63 [t (J = 6.5 Hz), 2H, $BrCH_2$], 3.65 [t, (J = 4.5 Hz), 4H, OCH_2], 8.68 (bs, 2H, NH_2); cmr (DMSO-d_6): δ ppm 30.3 (CCH_2C), 32.9 ($BrCH_2$), 33.2 (SCH_2), 45.2 (NCH_2), 65.6 (OCH_2), 157.5 (C-5), 162.2 (C-3), 193.6 (C=S); ms: M^+ = 366.

Anal. Calcd. for $C_{10}H_{16}BrN_5OS_2$ (MW 366.31): C, 32.79; H, 4.40; N, 19.12; S, 17.51; Br, 21.81. Found: C, 32.85; H, 4.56; N, 18.97; S, 17.48.

The crystals not soluble in hot acetonitrile were recrystallised twice from dioxane to yield 1.7 g (16%) of 1,3-propylene-bis (5-amino-3-morpholino-1*H*-1,2,4-triazol-1-yl)dithiocarbonate (**14**, Q = morpholino, n = 3), mp 243-245°; ir: ν NH_2 = 3340 and 3280 cm^{-1}, ν C=N = 1670 and 1571 cm^{-1}, ν C=S = 1276 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.07 [qi (J = 7 Hz), 2H, CCH_2C], 3.24 [t (J = 7 Hz), 4H, SCH_2], 3.36 [t (J = 4.3 Hz), 4H, NCH_2], 3.65 [t (J = 4.3 Hz), 4H, OCH_2], 8.68 (bs, 2H, NH_2); cmr (DMSO-d_6): δ ppm 25.7 (CCH_2C), 33.6 (SCH_2), 45.2 (NCH_2), 65.6 (OCH_2), 157.6 (C-5), 162.2 (C-3), 193.8 (C=S).

Anal. Calcd. for $C_{17}H_{26}N_{10}O_2S_4$ (MW 530.72): C, 38.47; H, 4.94; N, 26.39; S, 24.17. Found: C, 38.35; H, 5.08; N, 26.30; S, 24.23.

The combined mother liquors were evaporated *in vacuo* to dryness and the residue was chromatographed on a silica gel column (eluent a 3:1 mixture of chloroform and methanol) to yield 1.2 g (11%) of 2-morpholino-7,8,9,10-tetrahydro[1,2,4]triazolo[1,5-*c*]-[1,3,5]thiadiazocine-5-thione (**17**, Q = morpholino) that after recrystallisation from dimethylformamide melted at 254-257°; ir: ν NH = 3380 cm^{-1}, ν C=N = 1670 and 1580 cm^{-1}, ν C=S = 1280 cm^{-1}; pmr (DMSO-d_6): δ, ppm 2.15 (qi, 2H, CCH_2C), 3.30 (t, 2H, SCH_2), 3.38 (t, 4H, NCH_2), 3.57 (qa, 2H, $NHCH_2$), 3.65 (t, 4H, OCH_2), 10.5 (bs, 1H, NH); cmr (DMSO-d_6): δ ppm 21.0 (CCH_2C), 27.7 (SCH_2), 35.3 ($NHCH_2$), 45.8 (NCH_2), 65.6 (OCH_2), 158.9 (C-10a), 163.5 (C-2), 195.3 (C=S); ms: M^+ = 285.

Anal. Calcd. for $C_{10}H_{15}N_5OS_2$ (MW 285.40): C, 42.09; H, 5.30; N, 24.54, S, 22.47. Found: C, 42.11; H, 5.47; N, 24.49; S, 22.51.

(4-Bromobutyl) 5-Amino-3-methylthio-1*H*-1,2,4-triazol-1-yl-dithiocarbonate (**12**, Q = methylthio, n = 4).

To a solution of 5.30 g (0.04 mole) of 5-amino-3-methylthio-1*H*-1,2,4-triazole (**1**, Q = methylthio, R^1 = H) [6] in a mixture of 25 ml of dimethylformamide and 15 ml of water 2.52 ml (3.2 g, 0.042 mole) of carbon disulfide, the solution of 2.6 g (0.046 mole) of potassium hydroxide in 10 ml of water and 4.74 ml (8.64 g, 0.04 mole) of 1,4-dibromobutane (**10**), respectively, were added by dropping them to the reaction mixture with stirring below 10°. After standing at room temperature overnight 200 ml of water was added to the reaction mixture, the product was extracted twice with 150 ml portions of chloroform, the combined chloroform layers were washed with water, dried over anhydrous sodium sulfate and evaporated to dryness to yield 6.6 g (48%) of (4-bromobutyl) 5-amino-3-methylthio-1*H*-1,2,4-triazol-1-yl-dithiocarbonate (**12**, Q = methylthio, n = 4) which after recrystallisation from acetonitrile melted at 113-115°; ir: ν C=N = 1650 and 1595 cm^{-1}; ν C=S = 1270 cm^{-1}; pmr (DMSO-d_6): δ ppm 1.81 (qi, 2H, CH_2-3'), 1.92 (qi, 2H, CH_2-2'), 2.52 (s, 3H, SCH_3), 3.21 (t, 2H, SCH_2), 3.58 (t, 2H, $BrCH_2$), 8.65 (bs, 2H, NH_2); cmr (DMSO-d_6): δ ppm 13.1 (SCH_3), 25.8 (CH_2-3'), 31.6 (CH_2-2'), 34.0 ($BrCH_2$), 34.5 (SCH_2), 157.4 (triazole C-5), 162.7 (triazole C-3), 196.6 (C=S).

Anal. Calcd. for $C_8H_{13}BrN_4S_3$ (MW 341.32): C, 28.15; H, 3.84; N, 16.41; S, 28.18. Found: C, 28.06; H, 3.88; N, 16.55; S, 27.99.

(4-Bromobutyl) 5-Amino-3-morpholino-1*H*-1,2,4-triazol-1-yl-dithiocarbonate (**12**, Q = morpholino, n = 4) and 1,4-Butylenebis (5-Amino-3-morpholino-1*H*-1,2,4-triazol-1-yl)dithiocarbonate (**15**, Q = morpholino, n = 4).

To a solution of 6.76 g (0.04 mole) of 5-amino-3-morpholino-1*H*-1,2,4-triazole (**1**, Q = morpholino, R^1 = H) [7] in a mixture of 25 ml of dimethylformamide and 15 ml of water, 2.52 ml (3.2 g, 0.042 mole) of carbon disulfide, a solution of 2.6 g (0.046 mole) of potassium hydroxide in 10 ml of water and 4.74 ml (8.64 g, 0.04 mole) of 1,4-dibromobutane (**10**, n = 4), respectively, were added dropwise with stirring below 10°. After standing at room temperature overnight the crystals which precipitated were filtered off and washed with 50 ml of ethanol to yield 10.8 g of a material that was a mixture of (4-bromobutyl) 5-amino-3-morpholino-1*H*-1,2,4-triazol-1-yl-dithiocarbonate (**12**, Q = morpholino, n = 4)

and 1,4-butylenebis (5-amino-3-morpholino-1*H*-1,2,4-triazol-1-yl)-dithiocarbonate (**15**, Q = morpholino, n = 4). This was refluxed for 2 minutes with 75 ml of acetonitrile and filtered while hot. The filtrate crystallised upon cooling to yield 5.7 g, (38%) of (4-bromobutyl) 5-amino-3-morpholino-1*H*-1,2,4-triazol-1-yl-dithiocarbonate (**12**, Q = morpholino, n = 4) which after recrystallisation from dimethylformamide melted at 174-176°; ir: ν C=N = 1660 and 1590 cm^{-1}, ν C=S = 1280 cm^{-1}; pmr (DMSO-d_6): δ ppm 1.78 (qi, 2H, CH_2-3'), 1.93 (qi, 2H, CH_2-2'), 3.16 (t, 2H, SCH_2), 3.36 (t, 4H, NCH_2), 3.57 (t, 2H, $BrCH_2$), 3.65 (t, 4H, OCH_2), 8.68 (s, 2H, NH_2); cmr (DMSO-d_6): δ ppm 26.0 (CH_2-3'), 31.5 (CH_2-2'), 33.6 ($BrCH_2$), 34.2 (SCH_2), 45.2 (NCH_2), 65.5 (OCH_2), 157.3 (triazole C-5), 161.8 (triazole C-3), 193.8 (C=S); ms: M^+ = 380.

Anal. Calcd. for $C_{11}H_{18}BrN_5OS_2$ (MW 380.34): C, 34.74; H, 4.77; N, 18.41; S, 16.86. Found: C, 34.69; H, 4.70; N, 18.44; S, 16.95.

The crystals that were insoluble in acetonitrile were recrystallised twice from dioxane to yield 1.3 g (12%) of 1,4-butylenebis (5 amino-3-morpholino-1*H*-1,2,4-triazol-1-yl)dithiocarbonate (**15**, Q = morpholino, n = 4), mp 272-275°; ir: ν NH_2 = 3310 and 3200 cm^{-1}, ν C=N = 1657 cm^{-1}, ν C=S = 1306 cm^{-1}; pmr (DMSO-d_6): δ ppm 1.80 (m, 4H, CH_2-2' and CH_2-3'), 3.18 (t, 4H, SCH_2), 3.36 (t, 8H, NCH_2), 3.65 (t, 8H, OCH_2), 8.63 (bs, 4H, NH_2); cmr (DMSO-d_6 + deuteriochloroform): δ ppm 22.3 (CH_2-2' + CH_2-3'), 33.9 (SCH_2), 45.2 (NCH_2), 65.6 (OCH_2), 157.5 (C-5), 162.1 (C-3), 194.1 (C=S).

Anal. Calcd. for $C_{18}H_{28}N_{10}O_2S_4$ (MW 544.75): C, 39.69; H, 5.18; N, 25.71; S, 23.54. Found: C, 39.72; H, 5.25; N, 25.68; S, 23.61.

2-(3-Methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = methylthio, R^1 = 1-phenyl, n = 1).

To a solution of 10.3 g (0.05 mole) of 5-amino-3-methylthio-1-phenyl-1*H*-1,2,4-triazole (**1**, Q = methylthio, R^1 = 1-phenyl) [6] in 20 ml of dimethylformamide 3.95 g (3.2 ml = 0.052 mole) of carbon disulfide was added dropwise with stirring at room temperature followed by the addition of a solution of 5.6 g (0.1 mole) of potassium hydroxide in 6 ml of water. The mixture was stirred at 70° for 1 hour, cooled to room temperature, 8.7 g (3.5 ml = 0.05 mole) of dibromomethane was added and stirred at room temperature for a further 2 hours. After addition of 50 ml of water the crystals which precipitated were filtered off, washed with water and recrystallised from acetonitrile to yield 9.6 g (65%) of 2-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = methylthio, R^1 = 1-phenyl, n = 1), mp 149-150°; ir: ν C=N = 1572 and 1502 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.60 (s, 3H, SCH_3), 3.93 (s, 2H, CH_2), 7.30 (t, 1H, *p*-PhH), 7.43 (dt, 2H, *m*-PhH), 7.80 (dd, 2H, *o*-PhH); cmr (DMSO-d_6): δ ppm 13.4 (SCH_3), 19.4 (CH_2), 120.3, 124.0, 127.1 and 136.5 (Ph-C), 153.7 (triazole C-5), 158.9 (triazole C-3), 173.0 (S_2C=N).

Anal. Calcd. for $C_{11}H_{10}N_4S_3$ (MW 294.43): C, 44.87; H, 3.42; N, 19.03; S, 32.67. Found: C, 44.95; H, 3.31; N, 19.11; S, 32.69.

2-(1-Benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = morpholino, R^1 = 1-benzyl, n = 1).

This compound was prepared as that described for 2-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = methylthio, R^1 = 1-benzyl, n = 1) starting from 4.0 g (0.015 mole) of 5-amino-1-benzyl-3-morpholino-1*H*-1,2,4-triazole (**1**, Q = morpholino, R^1 = 1-benzyl) [7], yield 2.4 g (47%) of 2-(1-benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = morpholino, R^1 = 1-benzyl, n = 1), mp 137-138° (2-butanone); ir: ν C=N = 1577, 1556 and 1498 cm^{-1}; pmr (deuteriochloroform): δ ppm 3.35 (t, 4H, NCH_2), 3.75 (t, 4H, OCH_2), 3.89 (s, 2H, CH_2), 5.16 (s, 2H, $PhCH_2$), 7.3 (m, 5H, PhH); cmr (deuteriochloroform): δ ppm 17.9 (CH_2), 46.4 (NCH_2); 49.6 ($PhCH_2$), 66.2 (OCH_2), 127.4, 127.7, 128.4 and 136.9 (PhC), 153.0 (triazole C-5), 163.4 (triazole C-3), 166.8 (S_2C=N).

Anal. Calcd. for $C_{15}H_{17}N_5OS_2$ (MW 347.48): C, 51.85; H, 4.93; N, 20.16; S, 18.46. Found: C, 52.02; H, 4.71; N, 19.97; S, 18.37.

2-(3-Methylthio-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = methylthio, R^1 = H, n = 1).

This compound was prepared as that described for 2-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = methylthio, R^1 = 1-phenyl, n = 1) starting from 6.5 g (0.05 mole) of 5-amino-3-methylthio-1*H*-1,2,4-triazole (**1**, Q = methylthio, R^1 = H) [6], yield 6.6 g (61%) of 2-(3-methylthio-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = methylthio, R^1 = H, n = 1), mp 157-159° (acetonitrile); ir: ν C=N = 1566 and 1494 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.55 (s, 3H, SCH_3), 4.13 (s, 2H, CH_2), 13.7 (bs, 1H, NH); cmr (DMSO-d_6): δ ppm 13.8 (SCH_3), 18.6 (CH_2), 156.2 (triazole C-5), 158.6 (triazole C-3), 169.5 (S_2C=N).

Anal. Calcd. for $C_5H_6N_4S_3$ (MW 218.33): C, 27.50; H, 2.77; N, 25.66; S, 44.06. Found: C, 27.36; H, 2.76; N, 25.48; S, 44.18.

2-(3-Methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithiolane (**19**, Q = methylthio, R^1 = 1-phenyl, n = 2).

To a solution of 2.1 g (0.01 mole) of 5-amino-3-methylthio-1-phenyl-1,2,4-triazole (**1**, Q = methylthio, R^1 = H) [6] in 20 ml of dimethylformamide 0.76 g (0.6 ml = 0.001 mole) of carbon disulfide was added dropwise with stirring at room temperature. The mixture was cooled to 10° and at this temperature a solution of 1.2 g (0.022 mole) of potassium hydroxide in 4 ml of water was added dropwise with stirring. The temperature of the reaction mixture was allowed to raise with stirring to room temperature. After stirring for 1 hour 1.9 g (0.87 ml = 0.01 mole) of 1,2-dibromoethane was added dropwise and stirring at room temperature was continued for a further 2 hours. After adding 30 ml of water, yellow crystals precipitated from the reaction mixture that were collected, washed twice with 10 ml portions of water, then twice with cold methanol and dried at room temperature to yield 2.0 g (64%) of 2-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithiolane (**19**, Q = methylthio, R^1 = 1-phenyl, n = 2), mp 88-90°; ir: ν C=N = 1599, 1537 and 1501 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.65 (s, 3H, SCH_3), 3.59 (s, 4H, SCH_2), 7.30 (t, 1H, *p*-PhH), 7.43 (dt, 2H, *m*-PhH), 7.78 (dd, 2H, *o*-PhH); cmr (deuteriochloroform): δ ppm 14.2 (SCH_3), 36.7 (SCH_2), 122.8, 127.0, 128.7 and 137.5 (PhC), 154.5 (triazole C-5), 159.5 (triazole C-3), 183.4 (S_2C=N).

Anal. Calcd. for $C_{12}H_{12}N_4S_3$ (MW 308.45): C, 46.73; H, 3.92; N, 18.16; S, 31.19. Found: C, 46.60; H, 4.01; N, 18.10; S, 31.31.

2-(3-Methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithiane (**20**, Q = methylthio, R^1 = 1-phenyl, n = 3).

This compound was prepared as that described for 2-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = methylthio, R^1 = phenyl, n = 1) using 10.1 g (5.1 ml = 0.05 mole) of 1,3-dibromopropane (**9**), yield 8.4 g (52%) of 2-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)-imino-1,3-dithiane (**20**, Q = methylthio, R^1 = 1-phenyl, n = 3), mp 130-131° (acetonitrile); ir: ν C=N = 1595, 1537 and 1497 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.19 (qi, 2H, CCH_2C), 2.57 (s, 3H, SCH_3), 3.25 (t, 4H, SCH_2), 7.38 (t, 1H, *p*-PhH), 7.51 (dt, 2H, *m*-PhH), 7.66 (dd, 2H, *o*-PhH); cmr

(DMSO-d_6): δ ppm 13.5 (SCH_3), 21.9 (CCH_2C), 29.9 (SCH_2), 122.4, 127.1, 128.8 and 136.8 (PhC), 152.9 (triazole C-5), 158.6 (triazole C-3), 178.6 ($S_2C=N$).

Anal. Calcd. for $C_{13}H_{14}N_4S_3$ (MW 322.48): C, 48.42; H, 4.38; N, 17.37; S, 29.83. Found: C, 48.51; H, 4.44; N, 17.30; S, 29.79.

2-(1-Benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithiane (**20**, Q = morpholino, R^1 = 1-benzyl, n = 3).

This compound was prepared as that described for 2-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**18**, Q = methylthio, R^1 = phenyl, n = 1) starting from 2.59 g (0.01 mole) of 5-amino-1-benzyl-3-morpholino-1*H*-1,2,4-triazole (**1**, Q = morpholino, R^1 = 1-benzyl) [7] using 2.0 g (1.0 ml = 0.01 mole) of 1,3-dibromopropane (**9**), yield 1.7 g (45%) of 2-(1-benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithiane (**20**, Q = morpholino, R^1 = 1-benzyl, n = 3), mp 154-156° (2-butanone); ir: ν C=N = 1552 and 1521 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.24 (qi, 2H, CCH_2C), 3.10 (t, 4H, SCH_2), 3.38 (t, 4H, NCH_2), 3.78 (t, 4H, OCH_2), 5.20 (s, 2H, CH_2Ph), 7.25 (m, 5H, PhH); cmr (deuteriochloroform): δ ppm 22.6 (CCH_2C), 30.4 (SCH_2), 46.8 (NCH_2), 50.3 ($PhCH_2$), 66.5 (OCH_2), 127.4, 127.7, 128.4 and 136.9 (PhC), 152.5 (triazole C-5), 163.4 (triazole C-3), 174.0 ($S_2C=N$).

Anal. Calcd. for $C_{17}H_{21}N_5OS_2$ (MW 375.52): C, 54.37; H, 5.64; N, 18.65; S, 17.08. Found: C, 54.40; H, 5.89; N, 18.51; S, 16.91.

2-(4-Benzyl-3-methylthio-4*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**21**, Q = methylthio) and 1-Benzyl-2-methylthio-1,7-dihydro-5*H*-1,2,4-triazolo[1,5-*c*][1,3,5]thiadiazine-5-thione (**22**).

To a solution of 2.2 g (0.01 mole) of 5-amino-4-benzyl-3-methylthio-1,2,4-triazole [8] in 15 ml of dimethylformamide 0.9 g (0.72 ml = 0.012 mole) of carbon disulfide was added with stirring at room temperature followed by dropwise addition of a solution of 1.6 g (0.032 mole) of potassium hydroxide in 3 ml of water. The mixture was stirred at 60° for 1 hour. After cooling to room temperature 1.74 g (0.7 ml = 0.01 mole) of dibromomethane was added to the reaction mixture and stirred for further 1 hour. After addition of 20 ml of water to the reaction mixture it was extracted twice with 10 ml portions of chloroform, the combined organic layers were washed with water, dried over anhydrous sodium sulfate, evaporated *in vacuo* to dryness and the residue was recrystallised from acetonitrile to yield 0.6 g (20%) of 2-(4-benzyl-3-methylthio-4*H*-1,2,4-triazol-5-yl)imino-1,3-dithietane (**21**, Q = methylthio), mp 117-118°; ir: ν C=N = 1560 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.58 (s, 3H, SCH_3), 3.89 (s, 2H, CH_2), 5.02 (s, 2H, $PhCH_2$), 7.2-7.5 (m, 5H, PhH); cmr (deuteriochloroform): δ ppm 14.7 (SCH_3), 17.3 (CH_2), 45.9 ($PhCH_2$), 127.5, 127.9, 128.5 and 135.0 (PhC), 149.1 (triazole C-3), 156.1 (triazole C-5), 167.1 ($S_2C=N$).

Anal. Calcd. for $C_{12}H_{12}N_4S_3$ (MW 308.45): C, 46.73; H, 3.92; N, 18.16; S, 31.19. Found: C, 46.89; H, 3.82; N, 18.05; S, 31.37.

The mother liquor was evaporated *in vacuo* to dryness and the oily residue (1.9 g) was chromatographed on a silica gel column (eluent a 2:1 mixture of benzene and ethyl acetate) to yield 1.5 g (49%) of 1-benzyl-2-methylthio-1,7-dihydro-5*H*-1,2,4-triazolo[1,5-*c*][1,3,5]thiadiazine-5-thione (**22**), mp 210-212° (acetonitrile); ir: ν C=N = 1555, 1545 and 1500 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.58 (s, 3H, SCH_3), 5.08 (s, 2H, $PHCH_2$), 5.35 (s, 2H, SCH_2N), 7.3-7.6 (m, 5H, PhH); cmr (deuteriochloroform): δ ppm 15.7 (s, 2H, SCH_3), 47.5 (SCH_2N), 48.5 ($PhCH_2$), 127.9, 128.6, 129.1 and 135.8 (PhC), 150.4 (C-8a), 151.8 (C-2), 196.5 (C=S); ms: M^+ = 308.

Anal. Calcd. for $C_{12}H_{12}N_4S_3$ (MW 308.45): C, 46.73; H, 3.92; N, 18.16; S, 31.19. Found: C, 46.87; H, 4.06; N, 18.33; S, 31.38.

3-(3-Methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**24**, Q = methylthio, R^1 = 1-phenyl).

To a solution of 2.1 g (0.01 mole) of 5-amino-3-methylthio-1-phenyl-1*H*-1,2,4-triazole (**1**, Q = methylthio, R^1 = 1-phenyl) [6] in 10 ml of dimethylformamide 0.9 g (0.8 ml = 0.01 mole) of carbon disulfide was added dropwise with stirring at room temperature followed by addtition of a solution of 1.2 g (0.022 mole) of potassium hydroxide in 3 ml of water and stirring the mixture at 50° for 1 hour. After cooling to room temperature 1.9 g (0.9 ml = 0.01 mole) of 1,2-dibromoethane (**8**) was added dropwise to the reaction mixture and stirred again at 50° for 2 hours. After cooling the mixture was decomposed with 50 ml of water, the crystals which precipitated were collected, washed with water and recrystallised from ethanol to yield 2.1 g (69%) of 3-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**24**, Q = methylthio, R^1 = 1-phenyl), mp 109-111°; ir: ν C=N = 1591, 1543 and 1499 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.64 (s, 3H, SCH_3), 3.48 (dt, 2H, SCH_2), 3.62 (dt, 2H, NCH_2), 7.30 (t, 1H, *p*-PhH), 7.45 (dt, 2H, *m*-PhH), 7.80 (dd, 2H, *o*-PhH); cmr (deuteriochloroform): δ ppm 14.2 (SCH_3), 35.0 (SCH_2), 39.0 (NCH_2), 122.7, 126.9, 128.6 and 137.4 (PhC), 154.4 (triazole C-5), 159.4 (triazole C-3), 183.8 (C=S).

Anal. Calcd. for $C_{12}H_{12}N_4S_3$ (MW 308.45): C, 46.73; H, 3.92; N, 18.16; S, 31.19. Found: C, 46.65; H, 3.95; N, 18.09; S, 32.25.

3-(3-Methylthio-1-phenyl-1*H*-1,2,4-triazole-5-yl)thiazolidine-2-thione (**24**, Q = methylthio, R^1 = 1-phenyl) by Thermal Rearrangement of **19** (Q = methylthio, R^1 = phenyl, n = 2).

2-(3-Methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)imino-1,3-dithiolane (**19**, Q = methylthio, R^1 = 1-phenyl, n = 2) (7.7 g, 0.025 mole) was recrystallised from 120 ml of boiling ethanol. After cooling the crystals which precipitated were filtered off to yield 7.2 g (94%) of 3-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**24**, Q = methylthio, R^1 = 1-phenyl), mp 110-111°. The product is identical (mixed mp, ir) with that of **24** (Q = methylthio, R^1 phenyl) obtained above.

3-(1-Benzyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**25**, Q = methylthio, R^1 = 1-benzyl).

This compound was prepared as that described for 3-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**24**, Q = methylthio, R^1 = 1-phenyl) starting from 2.2 g (0.01 mole) of 5-amino-1-benzyl-3-methylthio-1*H*-1,2,4-triazole [6], yield 1.9 g (59%) of 3-(1-benzyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**25**, Q = methylthio, R^1 = 1-benzyl), mp 117-119° (acetonitrile); ir: ν C=N = 1668 and 1534 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.54 (s, 3H, SCH_3), 3.36 (dt, 2H, SCH_2), 3.50 (dt, 2H, NCH_2), 5.25 (s, 2H, $PhCH_2$), 7.25 (m, 5H, PhH); cmr (DMSO-d_6): δ ppm 14.2 (SCH_3), 34.2 (SCH_2), 39.1 (NCH_2), 50.2 ($PhCH_2$), 127.5, 127.6, 128.3 and 136.0 (PhC), 154.9 (triazole C-5), 158.7 (triazole C-3), 182.0 (C=S).

Anal. Calcd. for $C_{13}H_{14}N_4S_3$ (MW 322.48): C, 48.42; H, 4.38; N, 17.37; S, 29.83. Found: C, 48.57; H, 4.45; N, 17.31; S, 29.69.

3-(4-Benzyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**26**, Q = methylthio, R^1 = 4-benzyl).

This compound was prepared as that described for 3-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**24**, Q = methylthio, R^1 = 1-phenyl) starting from 2.2 g (0.01 mole) of 5-amino-4-benzyl-3-methylthio-1*H*-1,2,4-triazole [8], yield 1.7 g (53%) of 3-(4-benzyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**26**, Q = methylthio, R^1 = 4-benzyl, mp 148-150° (acetonitrile); ir: ν C=N = 1565 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.60 (s, 3H, SCH_3), 3.49 (t, 2H, SCH_2), 3.63 (t, 2H, NCH_2), 5.05 (s, 2H, $PhCH_2$), 7.2-7.3 (m, 5H, PhH); cmr (deuteriochloroform): δ ppm, 14.6 (SCH_3), 34.6 (SCH_2), 39.3 (NCH_2), 127.3, 127.6, 128.2 and 135.1 (PhC), 149.4 (triazole C-3), 155.9 (triazole C-5), 180.5 (C=S).

Anal. Calcd. for $C_{13}H_{14}N_4S_3$ (MW 322.48): C, 48.42; H, 4.38; N, 17.37; S, 29.83. Found: C, 48.68; H, 4.31; N, 17.08; S, 29.70.

3-(1-Benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**27**, Q = morpholino, R^1 = 1-benzyl).

This compound was prepared as that described for 3-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**24**, Q = methylthio, R^1 = 1-phenyl) starting from 2.6 g (0.01 mole) of 5-amino-1-benzyl-3-morpholino-1*H*-1,2,4-triazole [7], yield 2.1 g (58%) of 3-(1-benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)thiazolidine-2-thione (**27**, Q = morpholino, R^1 = 1-benzyl), mp 163-164° (ethanol); ir: ν C=N = 1570 and 1540 cm^{-1}; pmr (deuteriochloroform): δ ppm 3.25 (t, 4H, NCH_2), 3.70 (t, 4H, OCH_2), 5.17 (s, 2H, $PhCH_2$), 7.15-7.4 (m, 5H, PhH); cmr (deuteriochloroform): δ ppm 36.1 (SCH_2), 41.0 (NCH_2), 45.8 (NCH_2), 51.0 (CH_2Ph), 67.4 (OCH_2), 127.5, 127.6, 128.8 and 137.3 (PhC), 155.0 (triazole C-5), 164.5 (triazole C-3), 183.6 (C=S).

Anal. Calcd. for $C_{16}H_{19}N_5OS_2$ (MW 361.50): C, 53.16; H, 5.30; N, 19.37; S, 17.74. Found: C, 53.01; H, 5.35; N, 19.51; S, 17.47.

Acknowledgement.

The authors wish to express their thanks to Mrs. Zsoltné Biró and Mrs. Sándorné Sólyom for recording the ir spectra, to Mr. Attila Fürjes and Mr. István Pallagi for recording the nmr spectra, to Mrs. Lászlóné Zalavári for performing the elemental analyses and to Mrs. Laszloné Nyikos, Miss Tünde Jenei, Mrs. Tiborné Tóth and Mr. Károly Siklódi for technical assistance.

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