On Triazoles. XXII [1]. Synthesis of Dialkyl (3-Q-1,2,4-Triazol-5-yl)iminodithiocarbonates

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Isomeric dialkyl and diaralkyl[1-, 2- and 4-(alkyl, aralkyl and aryl)-3-Q-1,2,4-triazole-5-yl]iminodithiocarbonates **4a-c** (R ≠ H) were synthesised and their spectral data compared. The uv, cmr and ms rules elaborated helped to prove the tautomeric structure of the non-substituted derivatives **4** (R = H). In case of dimethyl (3-methylthio-1,2,4-triazole-5-yl)iminodithiocarbonate this is the first time ever crystalline triazole desmotropes **4a/17** and **4b/17** could be isolated. The sodium salts of **4** (R = H) could be further alkylated and aralkylated to yield the corresponding **4** (R = alkyl and aralkyl) type derivatives. Providing the above reaction in the presence of carbon disulfide the dithiocarbomethoxy derivative **7** was obtained.

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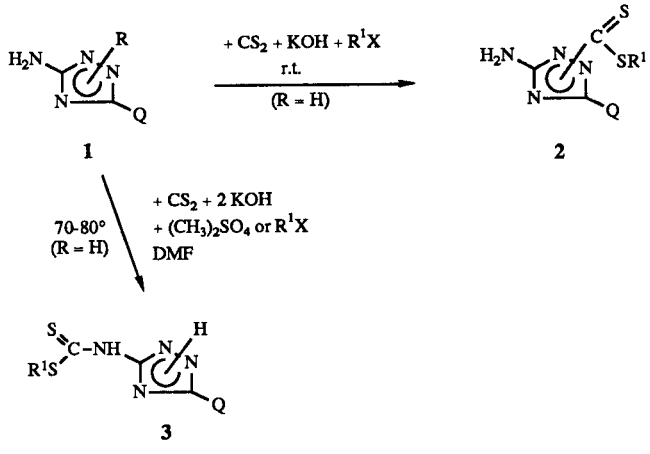
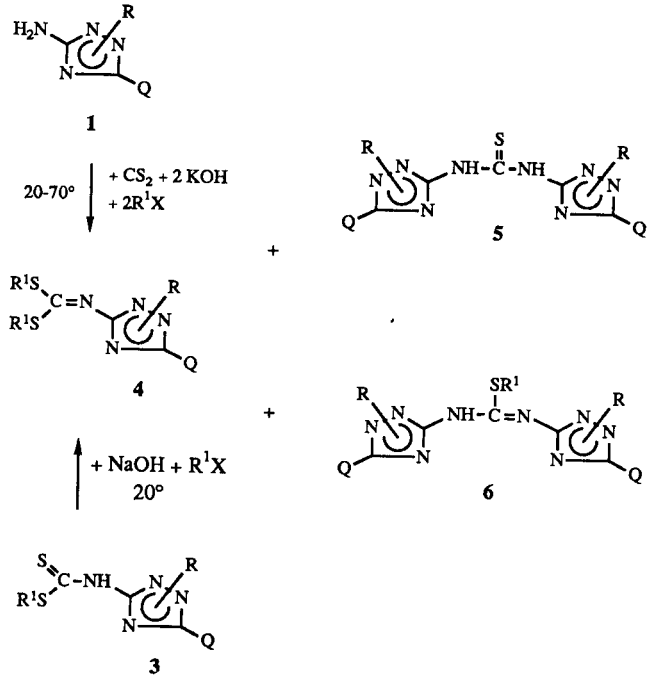
In the previous paper of this series [1] we have described the alkylation, aralkylation and arylation of different potassium 1,2,4-triazolyldithiocarbonates prepared from 5-amino-3-R²-thio- [2] and 5-amino-3-R²,R³-amino- [3] -1,2,4-triazole derivatives (**1**, Q = SR² and NR²R³, respectively), using carbon disulfide and potassium hydroxide with 1 mole of the corresponding alkyl, aralkyl and activated aryl halides to yield **2** type "ring dithiocarboxylated" aklyl, aralkyl or aryl (5-amino-3-Q-1,2,4-triazol-1-yl)dithiocarbonates and **3** type alkyl (5-amino-3-Q-1,2,4-triazol-5-yl)aminodithiocarbonates (Scheme 1).

Scheme 1



We will now report on the reaction of the dipotassium 1,2,4-triazolyliminodithiocarbonates prepared in the reaction of the above 5-amino-1,2,4-triazoles (**1**, R = H, alkyl, aralkyl, aryl, Q = SR², NR²R³), using carbon disulfide, and an excess of potassium hydroxide with 2 moles of the corresponding alkyl or aralkyl halides to yield the corresponding dialkyl or diaralkyl (3-Q-1,2,4-triazole-5-yl)-iminodithiocarbonates (**4**, R = H, alkyl, aralkyl, aryl, R¹ = alkyl, aralkyl, Q = SR², NR²R³, Table I) besides a small amount of the corresponding 1,3-bis-(3-Q-1,2,4-triazole-5-yl)thioureas **5** or 1,3-bis(3-Q-1,2,4-triazole-5-yl)-2-R¹-isothioureas **6** that were in some cases isolated. The iminodithiocarbonate derivatives **4** were also obtained by the further alkylation of the corresponding alkyl or aralkyl aminodithiocarbonates **3** synthesised recently [1] (Scheme 2).

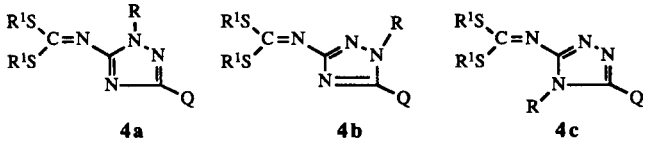
Scheme 2



Depending on the quality and the position of the R groups of the starting 5-amino-1,2,4-triazoles **1** derivatives **4** obtained may be represented either by the isomeric

structures **4a-4c** (R ≠ H) or the tautomers **4a-4c** (R = H) (Scheme 3).

Scheme 3



4a **4b** **4c**

The ir and pmr spectra of the isomers **4a-4c** (R ≠ H) (Table II) were in accordance with that of expected but except of **4a/16** and **4b/16** (Q = H) characterised by the triazole δ CH shifts were not characteristic for any of them (Table II).

The two uv maxima of isomers **4a**, **4b** and **4c** (R ≠ H) taken in ethanol appeared between 300-314 and 249-252 nm, 282-288 and 233-242 nm, and 296-299 and 250-252 nm, respectively (Table II), giving a possibility of easy dif-

Table I

Compound No./ Structure	R	Q	R^1	Conditions of Preparation X	Method	Yield (%)	mp (°) (Crystalized from)	Molecular Formula (MW)	Analysis Calcutated/Found C	H	N	S
4a/1	Methyl	Methylthio	Methyl	-	[1]	50	88-89 (EtOH)	$C_7H_{12}N_4S_3$ (248.40)	33.85 33.97	4.87 5.01	22.56 22.51	38.73 38.64
4a/2	Benzyl	Methylthio	Methyl	I	C [1]	34 58	103-105 (2-PrOH)	$C_{13}H_{16}N_4S_3$ (324.50)	48.12 48.22	4.97 5.11	17.27 17.16	29.65 29.60
4a/3	Phenyl	Methylthio	Methyl	I	C	82	95-97 (CH_3CN)	$C_{12}H_{14}N_4S_3$ (310.47)	46.42 46.35	4.55 4.63	18.05 18.11	30.98 30.93
4a/4	2,6-dimethyl-phenyl	Methylthio	Methyl	I	C	50	106-107 (EtOH)	$C_{14}H_{18}N_4S_3$ (338.52)	49.67 49.80	5.36 5.51	16.55 16.45	28.42 28.35
4a/5	Methyl	Morpholino	Methyl	-	[1]	65	114-116 (2-PrOH)	$C_{10}H_{17}N_5OS_2$ (287.41)	41.79 41.70	5.96 6.01	24.37 24.32	22.31 22.37
4a/6	Benzyl	Morpholino	Methyl	I	[1] [1]	71 67	128-129 (EtOH)	$C_{16}H_{21}N_5OS_2$ (363.51)	52.87 52.98	5.82 5.99	19.27 19.06	17.64 17.51
4a/7	Phenyl	Methylthio	Benzyl	Br	C	83	104-106 (CH_3CN)	$C_{24}H_{22}N_4S_3$ (462.67)	62.30 62.37	4.79 4.81	12.11 12.08	20.79 20.63
4b/8	Methyl	Methylthio	Methyl	I -	C [1]	17 [2] 24	77-78 (2-PrOH)	$C_7H_{12}N_4S_3$ (248.40)	33.85 33.92	4.87 4.95	22.56 22.50	38.73 38.68
4b/9	Propyl	Methylthio	Methyl	-	[1]	33	50-51 (CH:2-PrOH 4 : 1)	$C_9H_{16}N_4S_3$ (276.45)	39.10 38.99	5.83 5.80	20.27 20.43	34.80 34.68
4b/10	Benzyl	Methylthio	Methyl		[1]	12	90-91.5 (2-PrOH)	$C_{13}H_{16}N_4S_3$ (324.50)	48.12 48.03	4.97 5.02	17.27 17.33	29.65 29.82
4b/11	Methyl	Morpholino	Methyl	I	B [1]	44 [2] 10	102-103 (2-PrOH)	$C_{10}H_{17}N_5OS_2$ (287.41)	41.79 41.90	5.96 6.05	24.37 24.28	22.31 22.19
4b/12	Benzyl	Morpholino	Methyl		[1]	7	102-104 (EtOAc)	$C_{16}H_{21}N_5OS_2$ (363.51)	52.87 53.01	5.82 5.89	19.27 19.31	17.64 17.55
4c/13	Methyl	Methylthio	Methyl	I	A	10 [2]	100-102 (2-PrOH)	$C_7H_{12}N_4S_3$ (248.40)	33.85 33.67	4.87 4.90	22.56 22.63	38.73 38.88
4c/14	Benzyl	Methylthio	Methyl	I	C	63	145-147 (EtOH)	$C_{13}H_{16}N_4S_3$ (324.50)	48.12 48.01	4.97 5.05	17.27 17.34	29.65 29.70
4c/15	Phenyl	Methylthio	Methyl	I	C	78	137-139 (2-PrOH)	$C_{12}H_{14}N_4S_3$ (310.47)	46.42 46.55	4.55 4.67	18.05 17.92	30.98 30.88
4b/16 [3]	-	H	Methyl	I	B	51	153-155 (CH_3CN) Lit. [5] 152	$C_5H_8N_4S_3$ (188.28)	31.90 31.97	4.28 4.31	29.76 29.61	34.06 34.01
4a/17	-	Methylthio	Methyl				159-161 (CH_3CN)	$C_6H_{10}N_4S_3$ (234.37)	30.75 30.70	4.30 4.33	23.91 23.94	41.05 41.10
4b/17	-	Methylthio	Methyl	I	A	53	183-185 (EtOH)	$C_6H_{10}N_4S_3$ (234.37)	30.75 30.67	4.30 4.38	23.91 23.87	41.05 41.21
4a/18	-	Methylthio	Ethyl	I	A	55	104-106 (CH_3CN)	$C_8H_{14}N_4S_3$ (262.43)	36.62 36.53	5.38 5.21	21.35 21.53	36.66 36.82
4a/19	-	Methylthio	Benzyl	Br	A	68	130-132 (CH_3CN)	$C_{18}H_{18}N_4S_3$ (386.57)	55.93 56.05	4.69 4.71	14.49 14.46	24.89 24.99
4a/20 [4]	-	Ethylthio	Methyl	-	[5]	18	118-120 (2-PrOH)	$C_7H_{12}N_4S_3$ (248.40)	33.85 33.80	4.87 4.78	22.56 22.63	38.73 38.68

Table I (continued)

Compound No./ Structure	R	Q	R^1	Conditions of Preparation X	Method	Yield (%)	mp (°) (Crystalized from)	Molecular Formula (MW)	Analysis Calcutated/Found C	H	N	S
4a/21	-	Dimethyl-amino	Methyl	I	B	75	178-179	$C_7H_{13}N_5S_2$	36.34	5.66	30.27	27.72
				I	A	40 [6]	(2-PrOH)	(231.35)	36.40	5.77	30.30	27.65
				-	[5]	3						
4a/22 [7]	-	Dimethyl-amino	Methyl	I	B	71	137-138	$C_9H_{17}N_5S_2$	41.67	6.61	27.00	24.72
				I	A	38 [8]	(2-PrOH)	(259.40)	41.57	6.56	27.08	24.88
				-	[5]	2						
4a/23	-	Morpholino	Methyl	I	B	81	154-156	$C_9H_{15}N_5OS_2$	39.54	5.53	25.62	23.59
				I	A	51 [9]	(2-PrOH)	(273.38)	39.66	5.78	25.49	23.60
4a/24	-	Piperidino	Methyl	I	A	61	174-176 (2-PrOH)	$C_{10}H_{17}N_5S_2$ (271.41)	44.25 44.40	6.31 6.52	25.80 25.72	23.63 23.61

[1] see Experimental. [2] After chromatography on a silica-gel column, eluent a 2:1 mixture of benzene and ethyl acetate. [3] In solid state **4b/16**, in DMSO-d_6 solution 1:1 mixture of tautomeric forms **4a/16** and **4b/16** (pmr, cmr). [4] In DMSO-d_6 solution a 4:1 mixture of tautomeric forms **4a/20** **4b/20** (pmr). [5] Obtained as by-product of the reaction of the corresponding **1** (R = H) with CS_2, KOH and 0.1 mole of methyl iodide {see Lit [1]}. [6] By-product: **5** (Q = dimethylamino, R = H), mp 227-230° (DMF), M^+ = 296 ($C_9H_{16}N_{10}S$), ir, pmr, [7] In DMSO-d_6 solution a 4:1 mixture of tautomeric forms **4b/22** and **4a/22** (pmr). [8] By-product: **5** (Q = diethylamino, R = H), mp 210-212° (DMF), M^+ = 352 ($C_{13}H_{24}N_{10}S$), ir, pmr. [9] By-product: **5** (Q = morpholino, R = H), mp 268-270° (DMF), M^+ = 380 ($C_{13}H_{20}N_{10}O_2S$), ir, pmr.

Table II

Compound No./ Structure	ir [cm^{-1}] ν C = N	pmr [ppm] (DMSO-d_6) δ SCH_3 (3)	δ SCH_3 [1]	δ NH	other bands	cmr [ppm] (DMSO-d_6) δ C-3	δ C-5	δ $C(SR^1)_2$	uv λ max [nm] (ε. 10^{-3}) EtOH	10% EtOH + 90% 0.1 *N* HCl	10% EtOH + 90% 0.1 *N* NaOH
4a/1	1559	2.57 s	2.57 s		3.77 s	158.1	154.0	174.4 [2]	300 (9.5) 250 (12.6)	290 (8.2) 250 (12.2)	295 (7.8) 240 (12.3)
4a/2	1550	2.50 s 2.58 s	2.50 s 2.58 s		5.33 s 7.42-7.35	157.5	153.4	175.4	302 (9.0) 250 (12.3)	296 (8.0) 249 (12.2)	300 (7.6) 248 (11.8)
4a/3	1590 1540	2.59 s	2.55 s		7.5-7.7	160.5	154.7	179.0	312 (9.6) 250 (20.1)	304 (8.3) 248 (19.1)	304 (8.1) 248 (19.0)
4a/4	1590 1540	2.59 s	2.55 s		1.96 s 7.15-7.3	160.7	155.7	177.5	302 (10.6) 250 (16.0)	300 (9.8) 250 (15.0)	300 (9.3) 250 (14.3)
4a/5	1567 1530		2.55 s 2.58 s		3.21 t 3.62 s 3.66 t	164.2	153.6	174.4	311 (7.3) 249 (12.0)	298 (4.8) 251 (13.1)	306 (4.8)
4a/6	1570 1550		2.52 bs 2.59 bs		3.23 t 3.67 t 5.22 s 7.22-7.36 m	163.0	152.2	173.8	312 (7.5) 252 (12.3)	308 (4.9) 252 (12.3)	310 (8.5) 250 (11.2)
4a/7	1590	2.53 s			4.42 s 7.45-7.8 m	160.3	154.0	178.5	314 (9.6) 252 (20.7)	310 (8.7) 255 (10.2)	338 (6.2) 270 (7.5)
4b/8	1550	2.70 s	2.57 s		3.73 s	151.9	162.5	169.9 [2]	282 (8.1) 242 (13.7)	286 sh (10.5) 248 (12.1)	278 sh (6.4) 241 (14.7)
4b/9	1550	2.63 s	2.50 bs 2.55 bs		0.84 t 1.76 qa 3.93 t	151.2	162.0	169.5	288 (7.8) 240 (13.4)		
4b/10	1550	2.62 s	2.50 bs		5.22 s 7.25-7.37 m	151.7	162.2	169.9	281 (7.6) 241 (12.6)		
4b/11	1560		2.45 b 2.53 b		3.10 t 3.61 s 3.72 t	159.0	161.3	169.8	280 (6.8) 233 (22.2)	286 (10.8) 234 (12.6)	278 sh (5.2) 239 (8.6)

Table II (continued)

Compund No./ Structure	ir [cm^{-1}] ν C = N	pmr [ppm] (DMSO-d_6) δ SCH_3 (3)	δ SCH_3 [1]	δ NH	other	cmr [ppm] (DMSO-d_6) δ C-3 bands	δ C-5	δ $C(SR^1)_2$	uv λ max [nm] (ε. 10^{-3}) EtOH	10% EtOH + 90% 0.1 *N* HCl	10% EtOH + 90% 0.1 *N* NaOH
4b/12	1550		2.47 bs 2.55 bs		3.05 t 3.68 t 5.28 s 7.22- 7.40 m	157.6	160.4	168.9	282 (7.5) 236 (13.0)	290 (9.4) 239 (13.0)	280 (4.6)
4c/13	1500	2.60 s	2.57 bs 2.62 bs		3.46 s	148.7	154.8	173.0	298 (11.9) 252 (10.1)	287 (12.5) 260 (12.4)	294 (11.8)
4c/14	1550	2.59 s	2.49 bs 2.56 bs		5.08 s	149.2	155.0	174.0	296 (12.2) 251 (10.6)	288 (12.0) 258 (12.2)	292 (10.1) 245 (10.0)
4c/15	1570 1550	2.59 s			2.17 bs 2.60 bs 7.41- 7.56 m	149.1	154.4	173.6	299 (11.7) 250 (10.6)	290 (11.1) 257 (11.3)	295 (8.7) 248 (9.6)
4a/16 [3]	1580		2.52 bs	13.7 b	8.45 s	150.2	155.2	173.4	279 (8.9) 250 (10.4)	266 (12.5)	282 (6.0) 241 (9.3)
4b/16 [3]					7.85 s	143.0	163.1	168.9	280 (9.1) [4] 250 (9.8) [4]		
4a/17	1578	2.58 s 2.54 s	2.54 s 2.18 s	11.45 bs [5]		159.1	158.1	174.5	290 (8.7) 245 (13.3) 293 (9.8) [4] 247 (13.0) [4]	284 (11.0) 250 (12.7)	292 (6.0) 240 (13.1)
4b/17	1578	2.54 s	2.17 s	10.9 bs [5]					280 (9.4) [4] 245 (8.9) [4]		
4a/18	1581	2.62 s		12.5 b	3.12 qa 1.39 t	158.5	157.7	173.6	286 (9.2) 246 (11.1) 296 (10.0) [4] 253 (10.5) [4]	280 (11.9) 256 (11.2)	290 (4.2) 242 (14.1)
4a/19	1554	2.54 s			4.37 s 7.2- 7.4	159.3	157.6	172.8	284 (9.3) 250 (14.2) 303 (9.5) [4] 248 (12.9) [4]	299 (5.2) 240 (6.5)	300 (5.7) 244 (9.1)
4a/20 [6]	1580 1520		2.50 bs 2.56 bs	12.1 b	1.31 t 3.04 qa	157.4	155.6	174.0	288 (7.9) 244 (12.3) 302 (9.4) [4] 252 (11.7) [4]	286 sh (9.5) 250 (11.3)	290 (4.8)
4b/20 [6]			2.51 bs 2.52 bs	11.0 b							
4a/21	1620 1558		2.51 s	12.2 b	2.88 s	[7]	159.0	167.8	292 (7.2) 240 (22.3) 299 (10.1) [4] 247 (10.6) [4]	292 (8.8) 246 (9.2)	302 (7.4) 240 (21.0)
4a/22 [8]	1620 1560		2.47 s	12.0 b	1.08 t 3.34 qa	158.7	157.7	167.4	292 (7.6) 236 (24.8) 334 (5.9) [4] 249 (12.2) [4]	292 (9.3) 246 (9.9)	300 (6.4) 238 (20.8)
4b/22 [8]			2.51 s	11.9 b							
4a/23	1556		2.53 s		3.40 t 3.78 t	161.9	154.5	172.0	295 (5.4) 243 (13.8) 302 (8.0) [4] 251 (12.0) [4]	289 (6.6) 254 (10.2)	297 (3.9) 238 (11.7)
4a/24			2.51 s	12.3 b	1.53 bs 3.27 b				324 (5.4) [4] 260 (10.3) [4]		

[1] δ SCH_3 (ester). [2] Cmr taken in deuteriochlorform. [3] In DMSO-d_6 solution a 1:1 mixture of tautomers **4a/16** and **4b/16** (pmr). In Lit [1] described as **4c/16**. [4] Fresh solution in *n*-heptane. [5] Fresh solution in benzene-d_6. [6] In DMSO-d_6 solution a 4:1 mixture of **4a/20** and **4b/20** (pmr). [7] Not detected. [8] In DMSO-d_6 solution a 4:1 mixture of tautomers **4b/22** and **4a/22** (pmr).

ferentiation of derivatives **4b**. The differentiation between derivatives **4a** and **4c** made possible the relative intensities of the maxima. Thus is case of **4a** the maxima appearing at higher wavelengths were always much less intensive then those of their pairs appearing at lower ones. Just to the opposite, in case of derivatives **4c** from among

the pairs of maxima the more intensive was the one appearing at higher wavelengths.

Derivatives **4a-4c** could also be unequivocally differentiated with the help of their cmr and ms spectra. Thus the dithioester carbon atom of derivatives **4b** containing a "cross-conjugated" double bond system appeared consequently at about 169 ppm, while those of derivatives **4a** and **4c** representing a "linearily-conjugated" double bond system were shifted upfield to about 174 ppm. The differentiation between derivatives **4a** and **4c** made possible the triazole carbon atoms 3 that appeared in case of derivatives **4a** (as a consequence of the two pyridine-like nitrogen atoms attached) and **4c** (as a consequence of a pyridine-like and a pyrrole-like nitrogen atom attached) at about 160 and 149 ppm, respectively. On the other hand the analogues chemical surrounding of the triazole carbon atoms 5 of derivatives **4a** and **4c** resulted in their practically equivalent chemical shift of about 154 ppm, while in case of derivatives **4b** (where two pyridine-like nitrogen atoms were attached to it) an upfield shift was observed to about 162 ppm (Table II).

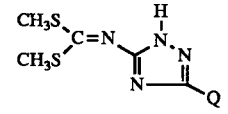
The ms spectra of derivatives **4a** were characterised with intensive molecular ions (M^+) and - as a consequence of the "linearly-conjugated" double bond system present - a main fragmentation pattern characterised by the fission of the R'-S-R' moiety from the dithioester group to yield a stable triazolyl-isothiocyanate ion $(M-[R'-S-R'])^+$. To the contrary the spectra of derivatives **4b** were characterised with rather weak molecular ions (M^+), and - as a consequence of the "cross-conjugated" double bond system present - weak triazolylisothiocyanate ions $(M-[R'-S-R'])^+$. In this case the loss of the SR' moiety to yield the $(M-SR')^+$ ions became dominant.

At last in the spectra of derivatives **4c** - as a consequence of the C=N-N=C arrangment of the "linearily-conjugated" double bond system present - the molecular ions $(M)^+$ were of medium intensity accompanied by the strong triazolylisothiocyanate ions $(M-[R'-S-R'])^+$. The cleavage of the Q-C=N moiety from the triazole ring became in this case to be dominat to yield the very intensive $(M-[R'S-C=N])^+$ peaks in the spectra of Q = alkylthio derivatives [4].

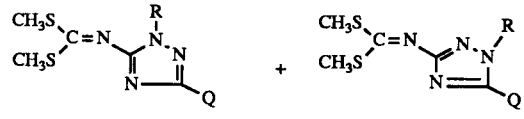
The above spectral data helped to prove the tautomeric structure of derivatives **4/16-4/24** (R = H). However, the uv measurements had to be repeated in fresh *n*-heptane solutions as in ethanol as solvent often different tautomeric equilibria developed. Thus the known derivative **4/16** (Q = H) described in Lit. [5] as **4c/16** exists in solid state and in *n*-heptane solution as **4b/16**, while in DMSO-d_6 solution as a 1:1 mixture of the tautomeric forms **4a/16** and **4b/16** (Table II).

The Q = methylthio derivatives **4/18-4/19** exists in solid state, *n*-heptane and DMSO-d_6 solutions in tautomeric

Scheme 4



4



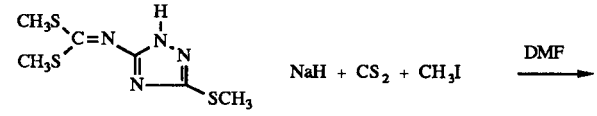
4a 4b

forms **4a/18** and **4a/19**. The Q = ethylthio derivative **4/20** exists in solid state and *n*-heptane solution as **4a/20**, while in DMSO-d_6 solution tautomeric equilibria occur. In ethanolic solution all three above mentioned derivatives appear as mixtures of tautomers (Table II).

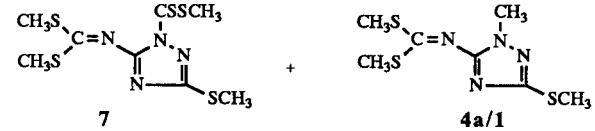
The Q = dialkylamino derivatives **4/21-4/24** exists in solid state and *n*-heptane solution in tautomeric forms **4a/21-4a/24** that tautomerises in ethanolic and DMSO-d_6 solutions to different tautomeric equilibria (Table II).

Quite unexpectidely the 3-methylthio-derivative **4/17** crystallised from the hot acetonitrile in the **4a/17** tautomeric form, while its slow crystallisation from dilute ethanol lead to the tautomeric form **4b/17** offering first time ever the possibility to isolate the crystalline triazole desmotropes. The rate of the interconversion of these tautomeric forms to an equilibric mixture was in DMSO-d_6 (pmr, cmr, Table II) and ethanolic (uv, Table II) solutions too high to distinquish them. However, they were stabile enough in fresh *n*-heptane and benzene-d_6 solutions to give a possibility to differentiante them by uv and pmr

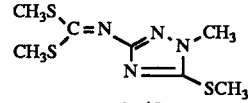
Scheme 5



4a/17



7 4a/1



4b/8

(Table II). Surprisingly, they could also be unequivocally distinquished by their ms spectra which followed consequently the rules elaborated by the study of the **4a, 4b** and **4c** (R = alkyl, aralkyl and aryl) type derivatives with fixed "tautomeric" structures [4].

The sodium salts of derivatives **4** (R = H) could also be further alkylated to yield **4a** and **4b** (R = alkyl, aralkyl) type compounds as proved by the methylation and benzylation experiments of derivatives **4a/17** or **4b/17** and **4a/23** (Scheme 4). On the other hand, if providing the above alkylation in the presence of 1 mole of carbon disulfide besides a small amount of the corresponding derivative **4a** and **4b** (R = alkyl) a further dithioester group was built in to the molecule to yield **7** (Scheme 5) the spectra of which were again in accordance with the rules elaborated for the corresponding alkyl triazolyldithiocarbonates **2a** [1] and dialkyl triazolyliminodithiocarbonates **4a** disscussed above.

EXPERIMENTAL

Melting points were determined on a Koffler-Boëtius micro apparatus and are uncorrected. The infrared spectra were obtained as potassium bromide pellets using Perkin-Elmer 577 spectrophotometer. The ultraviolet spectra were obtained by a Pye Unicam SP 8-150 instrument. The ^{1}H-nmr and the ^{13}C-nmr measurements were performed using Brucker WM-250 and Brucker WP-80 SY instruments. The ms spectra were recorded on a Kratos MS25RFA instrument using direct inlet probe.

General Methods for the Synthesis of Dialkyl (3-Q-1-R-1,2,4-Triazol-5-yl)iminodithiocarbonates **4**.

Method A.

To a solution of 0.1 mole of the corresponding 1-, 2- or 4-R-5-amino-3-Q-1,2,4-triazole **1** [2,3] in 50 ml of dimethylformamide 8.4 g (6.6 ml = 0.11 mole) of carbon disulfide was added dropwise with stirring, then the solution of 11.2 g (0.2 mole) of potassium hydroxide in 12 ml of water was added to the mixture and stirred at 70° for 2 hours. After cooling to the room temperature 0.2 mole of the corresponding alkyl or aralkyl halide (Table I) was added to the reaction mixture, stirred for further 2 hours, then 30 ml of water was added, the crystals precipitated were filtered off, washed with water and cold methanol and recrystallised from an appropriate solvent (Tables I and II).

Method B.

To a solution of 0.4 g (0.01 mole) of sodium hydroxide in 15 ml of water 0.01 mole of the corresponding alkyl (1-, 2- or 4-R-5-amino-3-Q-1,2,4-triazol-1-yl)aminodithiocarbonate (**3**) was added with stirring at room temperature. After the solid was dissolved 0.012 mole of the corresponding alkyl halide was added dropwise to the solution keeping its temperature below 30°. The stirring was continued at room temperature for 2 hours, the precipitated crystals were filtered off, washed with water and recrystallised from an appropriate solvent (Tables I and II).

Method C.

To a solution of 0.1 mole of the corresponding 1-, 2- or 4-R-5-amino-3-Q-1,2,4-triazole (**1**) [3,4] in 30 ml of dimethylformamide 8.4 g (6.6 ml = 0.11 mole) of carbon disulfide was dropped with stirring, then the solution of 11.2 g (0.2 mole) of potassium hydroxide in 12 ml of water was added to the mixture by dropping it with stirring and cooling keeping the temperature of the reaction mixture below 15°. After stirring the reaction mixture at the above temperature for 30 minutes 0.2 mole of the corresponding alkyl or aralkyl halide (Table I) was added keeping the temperature of the reaction mixture below 15°. The reaction was completed by stirring the mixture at room temperature for 2 hours, then 30 ml of water was added, the crystals precipitated were filtered off, washed with water and cold methanol and recrystallised from an appropriate solvent (Tables I and II).

Dimethyl (1-Benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/6**).

To a mixture of 0.7 g (0.023 mole) of sodium hydride (80% solution in paraffin oil, Fluka) and 7 ml of absolute dimethylformamide 2.6 g (0.01 mole) of 1-benzyl-3-morpholino-1*H*-1,2,4-triazole (**1**, R = benzyl) [3] was added in small portions with stirring below 10°. The mixture was stirred a further 10 minutes keeping its temperature at 10°, then 0.9 g (0.75 ml, 0.012 mole) of carbon disulfide was added dropwise to it and again stirred for 30 minutes. Then 2.8 g (1.3 ml, 0.02 mole) of methyl iodide was added dropwise to it and stirred for 8 hours at room temperature. The mixture was decomposed with 20 ml of water, the precipitated crystals were collected and recrystallised from ethanol to yield 2.5 g (71%) of dimethyl (1-benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/6**), mp 128-129° (ethanol) (Tables I and II).

Dimethyl (2-Propyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/9**).

To a solution of 0.86 g (0.005 mole) of 2-propyl-3-methylthio-2*H*-1,2,4-triazole (**1**, R = 2-propyl) in 6 ml of dimethylformamide 0.36 g (0.012 mole) of sodium hydride (80% solution in paraffin oil, Fluka) was added with stirring at room temperature. After the evolution of the hydrogen gas was ceased 0.4 ml (0.006 mole) of carbon disulfide was added dropwise to the reaction mixture below 20°. The mixture was stirred at room temperature for 30 minutes, then 0.8 ml (0.013 mole) of methyl iodide was added dropwise to it and stirred for further 60 minutes. The reaction mixture was decomposed with 20 ml of water and extracted twice with 20 ml portions of chloroform. The combined chloroform layers were washed with water, dried over sodium sulfate and evaporated *in vacuo* to dryness. The oily residue (0.9 g) was chromatographed on a silica gel column (eluent a 2:1 mixture of benzene and ethyl acetate) to yield 0.45 g (33%) of dimethyl (2-propyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/9**), which after recrystallisation from a 4:1 mixture of cyclohexane and 2-propanol melted at 50-51° (Tables I and II).

Dimethyl (1-Methyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/1**) and Dimethyl (2-Methyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/8**).

To a mixture of 0.7 g (0.023 mole) of sodium hydride (80% solution in paraffin oil, Fluka) and 15 ml of absolute dimethylformamide 4.7 g (0.02 mole) of dimethyl (3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/17** or **4b/17**) was added in small portions with stirring at 20°. After stirring the reaction mixture at 25-30° for 30 minutes 3.26 g (1.43 ml = 0.023 mole) of methyl iodide was dropped to the reaction mixture and stirred

for further 5 hours at room temperature. The crystals precipitated after the addition of 30 ml of water were filtered off and recrystallised from ethanol to yield 2.5 g (50%) of dimethyl (1-methyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/1**), mp 88-89° (Tables I and II).

The dimethylformamide-water containing mother liquor was extracted three times with 20 ml portions of chloroform, the combined chloroform layers were washed with water, dried and evaporated *in vacuo* to dryness. The oily residue was trituated with ether, the crystals precipitated were filtered off and recrystallised from acetonitrile to yield 1.2 g (24%) of dimethyl (2-methyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/8**), mp 77-78° (Tables I and II).

Dimethyl (1-Methyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/5**) and Dimethyl (2-Methyl-3-morpholino-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/11**).

To a mixture of 0.7 g (0.023 mole) of sodium hydride (80% solution in paraffin oil, Fluka) and 20 ml of absolute dimethylformamide 5.2 g (0.019 mole) of dimethyl (3-morpholino-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/23**) was added in small portions with stirring below 25°. After stirring the reaction mixture at 25° for 30 minutes 3.26 g (1.43 ml = 0.023 mole) of methyl iodide was added dropwise to the reaction mixture with stirring and cooling below 20° and the stirring was continued at room temperature for further 2 hours. The crystals precipitated after the addition of 30 ml of water were filtered off and recrystallised from 2-propanol to yield 3.55 g (65%) of dimethyl (1-methyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/5**), mp 114-116° (Tables I and II).

The dimethylformamide-water containing mother liquor was extracted two times with 20 ml portions of chloroform, the combined chloroform layers were washed with water, dried and evaporated *in vacuo* to dryness. The oily residue (1.35 g) was chromatographed on a silica gel column (eluent a 2:1 mixture of benzene and ethyl acetate) to yield 0.55 g (10%) of dimethyl (2-methyl-3-morpholino-2*H*-1,2,4-triazol-5-yl)-iminodithiocarbonate (**4b/11**), which after recrystallisation from 2-propanol melted at 102-103° (Tables I and II).

Dimethyl (1-Benzyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/2**) and Dimethyl (2-Benzyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/10**).

To a mixture of 1.08 g (0.036 mole) of sodium hydride (80% solution in paraffin oil, Fluka) and 25 ml of absolute dimethylformamide 7.02 g (0.03 mole) of dimethyl (3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/17** or **4b/17**) was added in small portions with stirring below 25°. After stirring the reaction mixture at 25° for 30 minutes 4.56 g (4.15 ml = 0.036 mole) of benzyl chloride was dropped to the reaction mixture with stirring and cooling below 20° and the stirring was continued at room temperature for further 2 hours. The reaction mixture was decomposed with 20 ml of water, extracted twice with 25 ml portions of chloroform, the combined chloroform extracts were washed with water, dried over sodium sulfate and evaporated to dryness. The residue (8.25 g) was dissolved in 25 ml of 2-propanol and let to crystallise. The crystals precipitated were collected to yield 4.2 g (43%) of dimethyl (1-benzyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/2**), mp 103-105° (Tables I and II).

The mother liquor was evaporated *in vacuo* to dryness and the oily residue (3.7 g) was chromatographed on a silica gel column (eluent a 2:1 mixture of benzene and ethyl acetate) to yield first a further crop of dimethyl (1-benzyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)-iminodithiocarbonate (**4a/2**) [1.5 g (15%), mp 103-105° (2-propanol)] then 1.2 g (12%) of dimethyl (2-benzyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/10**), which after recrystallisation from 2-propanol melted at 90-91.5° (Tables I and II).

Dimethyl (1-Benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/6**) and Dimethyl (2-Benzyl-3-morpholino-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/12**).

To a mixture of 0.7 g (0.023 mole) of sodium hydride (80% solution in paraffin oil, Fluka) and 20 ml of absolute dimethylformamide 5.48 g (0.02 mole) of dimethyl (3-morpholino-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/23**) was added in small portions with stirring below 25°. After stirring the reaction mixture at 25° for 30 minutes 3.93 g (3.45 ml = 0.023 mole) of benzyl bromide was dropped to the reaction mixture with stirring and cooling below 20° and the stirring was continued at room temperture for further 2 hours. The crystals precipitated after the addition of 20 ml of water were filtered off and recrystallised twice from ethanol to yield 4.9 g (6.7%) of dimethyl (1-benzyl-3-morpholino-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/6**), mp 128-129° (Tables I and II). The combined mother liquors were evaporated *in vacuo* to dryness and the residue (1.4 g) was chromatographed on a silica gel column (eluent a 2:1 mixture of benzene and ethyl acetate) to yield 0.55 g (7%) of dimethyl (2-benzyl-3-morpholino-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/12**), which after recrystallisation from ethyl acetate melted at 102-104° (Tables I and II).

Dimethyl (2-Methyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/8**) and 1,3-Bis-(2-methyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)thiourea (**5b/8**, R = 2-methyl, Q = methylthio).

To a mixture of 0.7 g (0.022 mole) of sodium hydride (80% solution in paraffin oil, Fluka) and 10 ml of absolute dimethylformamide 2.8 g (0.02 mole) of 5-amino-2-methyl-3-methylthio-1*H*-1,2,4-triazole (**1**, R = 2-methyl) [2] was added in small portions with stirring at 20°. The reaction mixture was stirred for 15 minutes at 15°, then 1.68 g (1.4 ml = 0.022 mole) of carbon disulfide was added to it, the stirring was continued for further 15 minutes and finally 8.5 g (3.7 ml = 0.06 mole) of methyl iodide was dropped to it as a consequence of which its temperature arose to 50°. The reaction was completed by stirring the mixture at this temperature for further 30 minutes. The crystals precipitated after the addition of 10 ml of water were filtered off, washed with water and recrystallised from a acetonitrile to yield 1.9 g (24%) of 1,3-bis-(2-methyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)thiourea (**5b/8**, R = 2-methyl, Q = methylthio), mp 205-206°; ir: ν NH = 3200-2700 cm^{-1}, ν C=N= 1590 and 1560 cm^{-1}, ν C=S = 1270 cm^{-1}; pmr (deuteriochloroform): δ ppm 2.66 (s, 6H, SCH_3), 3.72 (s, 6H, NCH_3), 11.3 (bs, 2H, NH); cmr (deuteriochloroform): δ ppm 17.0 (SCH_3), 36.9 (NCH_3), 153.6 (triazole C^5), 157.3 (triazole C^3), 180.4 (C=S); uv (ethanol): λ max nm ($\epsilon.10^{-3}$) 217 (20.7), 274 (20.4).

Anal. Calcd. for $C_9H_{14}N_8S_3$ (MW 330.44): C, 32.71; H, 4.27; N, 33.91; S, 29.11. Found: C, 32.87; H, 4.41; N, 33.74; S, 28.96.

The dimethylformamide-water containing mother liquor was extracted twice with chloroform, the combined chloroform layers were washed with water, dried and evaporated *in vacuo* to dryness. The oily residue (3.9 g) was triturated with ether, the

crystals precipitated were filtered off and recrystallised from acetonitrile to yield 2.65 g (53%) of dimethyl (2-methyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4b/8**), mp 77-78° (Tables I and II).

Dimethyl (3-Methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/3**) and 1,3-Bis-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)-2-methylisothiourea (**6a/3**, R = 1-phenyl, R^1 = methyl, Q = methylthio).

To a solution of 103.2 g (0.5 mole) of 5-amino-3-methylthio-1-phenyl-1*H*-1,2,4-triazole (**1**, R = 1-phenyl) [2] in 100 ml of dimethylformamide 41.9 g (33.1 ml = 0.55 mole) of carbon disulfide was added with stirring at room temperature followed by the addition of a solution of 61.7 g (1.1 mole) of potassium hydroxide in 40 ml of water at 30-35°. After stirring the reaction mixture for 30 minutes 141.9 g (62.3 ml = 1 mole) of methyl iodide was added with cooling keeping the temperature of the reaction mixture between 30-35° and the reaction was completed by stirring the reaction mixture at 80° for 1 hour. The crystals precipitated after the addition of 200 ml of water to the reaction mixture were filtered off, washed with water and dried. The product was dissolved in 400 ml of hot acetonitrile, the unsoluble part was filtered off and the solution was let to crystallise. The crystals precipitated were filtered off and washed with acetonitrile to yield 105 g (67%) of dimethyl (3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/3**), mp 95-97° (for its spectra data see Table II). The crystals unsoluble in hot acetonitrile were recrystallised from 20 ml of hot dimethylformamide to yield 8.5 g (7%) of 1,3-bis-(3-methylthio-1-phenyl-1*H*-1,2,4-triazol-5-yl)-2-methylisothiourea (**6a/3**, R = 1-phenyl, R^1 = methyl, Q = methylthio), mp 170-172°; ir: ν C=N = 1610 and 1590 cm^{-1}; pmr (DMSO-d_6): δ ppm 2.40 (s, 3H, SCH_3), 2,48 (s, 3H, SCH_3), 2.50 (s, 3H, SCH_3), 7.5-7.7 (m, 10H, ArH), 12.0 (b, 1H, NH); cmr (DMSO-d_6): δ ppm 13.4 (SCH_3), 14.6 (SCH_3), 150.3 (isothiourea), 158.0 (triazole C^5), 162.5 (triazole C^3); uv (ethanol): λ max nm ($\epsilon.10^{-3}$) 248 (24.0), 314 (16.5).

Anal. Calcd. for $C_{20}H_{20}N_8S_3$ (MW 468.68): C, 51.25; H, 4.30; N, 23.92; S, 20.53. Found: C, 51.39; H, 4.44; N, 23.75; S, 20.37.

Dimethyl (1-Dithiocarbomethoxy-3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**7**).

To a mixture of 2.1 g (0.066 mole) of sodium hydride (80% solution in paraffin oil, Fluka) and 60 ml of absolute dimethylformamide 14.1 g (0.06 mole) of dimethyl (3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**4a/17** or **4b/18**) was added in small portions with stirring at 15-20°. The reaction mixture was stirred for 15 minutes at 15°, then 5.1 g (3.9 ml = 0.066 mole) of carbon disulfide was added to the reaction mixture keeping its temperature at 15° and the stirring was continued for further 30 minutes. Then 8.5 g (3.7 ml = 0.06 mole) of methyl iodide was dropped to the reaction mixture at 15° and the stirring was continued for further 3 hours at room temperaure. The crystals precipitated after the addition of 60 ml of water were filtered off, washed with water and recrystallised from a 3:1 mixture of acetonitrile and dimethylformamide to yield 11.5 g (59%) of dimethyl (1-dithiocarbomethoxy-3-methylthio-1*H*-1,2,4-triazol-5-yl)iminodithiocarbonate (**7**), mp 158-159°; ir: ν C=N = 1566 cm^{-1}; pmr (DMSO-d_6): δ, ppm 2.63 (s, 6H, SCH_3), 2.64 (s, 3H, SCH_3), 2.71 (s, 3H, SCH_3), cmr (DMSO-d_6): δ ppm 16.0, 17.2 and 19.3 (SCH_3), 160.6 (triazole C-5), 162.1 (triazole C-3), 176.1 [($C(SCH_3)_2$], 196.8 ($CSSCH_3$); uv (ethanol): λ max nm ($\epsilon.10^{-3}$) 228 sh (9.8), 298 (19.0), 312 sh (16.8), 350 (11.9).

Anal. Calcd. for $C_8H_{12}N_4S_5$ (MW 324.51): C, 29.61; H, 3.73; N, 17.26; S, 49.40. Found: C, 29.87; H, 3.81; N, 17.08; S, 49.19.

The mother liquors were evaporated to dryness and the oily residue (3.1 g) was chromatographed on a silica gel column (eluent a 2:1 mixture of benzene and ethyl acetate) to yield 1.3 g (9%) of dimethyl (1-methyl-3-methylthio-1*H*-1,2,4-triazol-5-yl)-iminodithiocarbonate (**4a/1**) mp 88-89° (ethanol) which was identical (ir, mixed mp) with that of **4a/1** obtained above and 0.6 g (4%) of dimethyl (2-methyl-3-methylthio-2*H*-1,2,4-triazol-5-yl)-iminodithiocarbonate (**4b/8**) mp 76-78° (acetonitrile) which was identical (ir, mixed mp) with that of **4b/8** obtained above.

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