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PREPARATION AND REACTIVITY OF MESOIONIC 1,2,4-TRIAZOLO-[4,3-b]-1,2,4-TRIAZOLE DERIVATIVES[1].

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Abstract: A number of mesoionic compounds (2) derivatives of the 1,2,4-triazolo[4,3-b]-1,2,4-triazole ring system have been prepared from 4-amino-1-methyl-3,5-bis(methylthio)-1,2,4-triazolium cation and aryl isothiocyanates. Compounds (2) react with methyl iodide to give the methiodides (3) which undergo ring opening to the monocyclic compounds (4) through sulfur extrusion under thermal conditions. Methiodides (3) by sequential treatment with malononitrile and hydrochloric acid lead to the pyrazolo[5,1-c]-1,2,4-triazole (6).

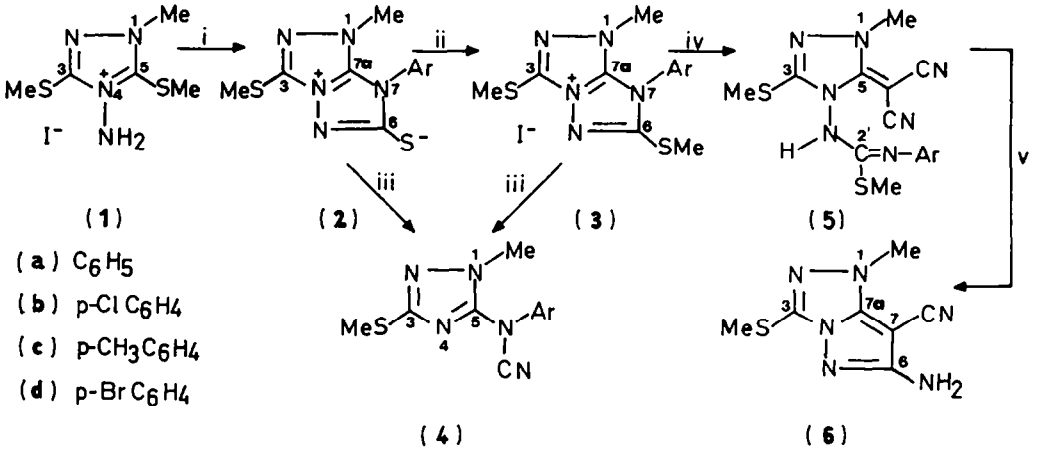
Our interest in the preparation of bridgehead nitrogen heterocycles bearing the 1,2,4-triazole moiety has encouraged us to look for specific routes to derivatives of 1H-1,2,4-triazolo[4,3-b]-1,2,4-triazole. In this context, we have reported the preparation of 6-aryl-1H-1,2,4-triazolo[4,3-b]-1,2,4-triazoles 1,3-disubstituted from 4-amino-1,2,4-triazoles 3,5-disubstituted and aromatic nitriles under basic conditions[2,3], and the preparation and characterization of mesoionic compounds derived from the 1,2,4-triazolo[4,3-b]-1,2,4-triazole ring system[4]. On the other hand, we have reported[5] that the reaction of 1-amino-2-methylthio-4,6-diphenylpyridinium cation with aryl isothiocyanates leads to 1,3,4-triazolo[3,2-a]pyridine derivatives which display mesoionic character.

The structural similarity between the 1-amino-2-methylthio-4,6-diphenylpyridinium cation and the heterocycle 4-amino-1-methyl-3,5-bis(methylthio)-1,2,4-triazolium cation (1) is such that this N-amino heterocycle might be expected to be suitable starting material for the preparation of fused mesoionic derivatives of the 1,2,4-triazolo[4,3-b]-1,2,4-triazole ring system. We report here attempts to synthesize anhydro 7-aryl-6-mercapto-1,2,4-triazolo[4,3-b]-1,2,4-triazole hydroxides (2).

4-Amino-1-methyl-3,5-bis(methylthio)-1,2,4-triazolium iodide (1), readily available from 4-amino-3,5-bis(methylthio)-1,2,4-triazole and methyl iodide[6], reacts with aryl isothiocyanates in dimethylformamide in the presence of triethylamine at room temperature for 24 h to yield the new mesoionic compounds anhydro 7-aryl-1-methyl-3-methylthio-6-mercapto-1,2,4-triazolo[4,3-b]-1,2,4-triazole hydroxides (2) as crystalline solids in high yields (70-80%). However, when the reaction is

carried out under ultrasonic irradiation, the reaction is completed in only 6 h. Support for the formulation **(2)** is clearly provided by their spectral data. The i.r. spectra show absorption at 1365 cm^{-1} attributable to thione stretching similar position to the thione stretching shown in the monocyclic anhydro 3-mercapto--1,2,4-triazolium hydroxides[7]. In the ^{1}H-n.m.r. spectra the chemical shifts of N-methyl and S-methyl groups are characteristic at δ 3.4-3.7 and δ 2.7-2.8 ppm respectively. Moreover, for (**2a**, Ar=C_6H_5) the phenyl group appears as a singlet which is characteristic of a phenyl out-of-plane. In the mass spectra of compounds **(2)** the expected molecular ion peak does not appear being the more significative-peaks due to the M^+-32 and to the 1-methyl-3-methylthio-1,2,4-triazole at m/z 128. Compounds **(2)** react with methyl iodide in dry benzene at room temperature to give the corresponding methiodides **(3)** as crystalline solids in excellent yields (77-81%).

When compounds **(2)** or **(3)** are heated above their melting points under nitrogen for a short period of time they are transformed into the monocyclic compounds **(4)** in high yields (69-78%). Similar results can be achieved when a solution of compound **(2)** or **(3)** in benzene is refluxed for 3 h. The i.r. spectra of compounds **(4)** show a strong absorption band at 2248 cm^{-1} due to the cyano group stretching and mass spectra show the expected molecular ion peak.

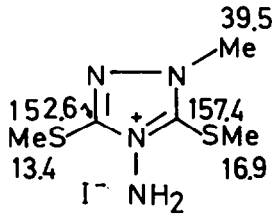


Methiodides **(3)** react with malononitrile under non-hydrolytic solid-liquid phase transfer catalysis using solid KF(base)/TEBA(catalyst)[8], to give the corresponding functionalised heterocyclic enamines **(5)** in good yields (61-68%). The i.r. spectra of compounds **(5)** show two strong absorption bands at 2200 and 2170 cm^{-1} respectively, attributable to C≡N stretching, the presence of the secondary amino group is confirmed by the absorption band around 3200 cm^{-1}. Mass spectra show the expected molecular ion peak and the fragmentation pattern is according with the proposed structure.

Compounds **(5)** by action of hydrochloric acid undergo hydrolytic cleavage followed by cyclization to give the same pyrazolo[5,1-c]-1,2,4-triazole **(6)** in high yield.

Carbon-13 n.m.r. study

Carbon-13 n.m.r. spectra were recorded in order to check the previous structures (2-6). Thanks to the fact that four different aryl substituents were synthesized, the assigment of aromatic carbons was straighforward. The other signals were assigned using previous results on 1,2,4-triazoles [4] and on aromatic azapentalenes [4,10] The starting material (1) is reported below.



(1)

The 1,2,4-triazolo[4,3-b]-1.2.4-triazoles (2) and (3) are reported in Table 1.

Table 1. Carbon-13 chemical shifts of 1,2,4-triazolo[4,3-b]-1,2,4-triazoles.

Compound	C_3	C_6	C_{7a}	N_1-CH_3	C_3-SMe	C_6-SMe	C_i	C_o	C_m	C_p
(2a)	136.3	175.9	144.6	35.8	13.6	---	131.6	128.4	128.8	129.4
(2b)	136.3	176.1	144.8	35.9	13.6	---	130.5	130.3	128.9	134.0
(2c)	136.4	n.o.	144.4	35.8	13.6	---	129.0	128.1	129.3	139.0[a]
(2d)	136.3	175.7	144.5	35.9	13.6	---	130.9	130.5	131.8	122.7
(3a)	138.6	162.3	146.1	36.6	14.2*	14.4*	128.2	127.3	130.4	132.0
(3b)	138.9	162.4	146.3	36.8	14.3*	14.6*	127.2	129.6	130.7	136.9
(3c)	138.6	162.5	146.2	36.5	14.1*	14.3*	125.6	127.0	130.7	142.1[b]
(3d)	138.7	162.2	146.0	36.7	14.2*	14.5*	127.4	129 5	133.5	125.6

[a] C_p-Me: 20.7; [b] C_p-Me: 20.8; *These assignments can be reversed.

As it can be seen pairs of compounds (2-3) have similar chemical shifts unless C_6;- the deshielding of this carbon in the betaines corresponds to a large thione (C=S) structure of the C_6-S^- bond. A more close examination shows small, but systematic, differences in phenyl chemical shifts, going from the betaine (2) to the quaternary salt (3) C_i∿-3 ppm, C_o∿-1 ppm, C_m∿+1.5 ppm and C_o∿+3 ppm. This is not- due to an steric effect, that would affect mainly C_o and C_m , but to a modification of electronic demand of the triazolotriazole substituent.

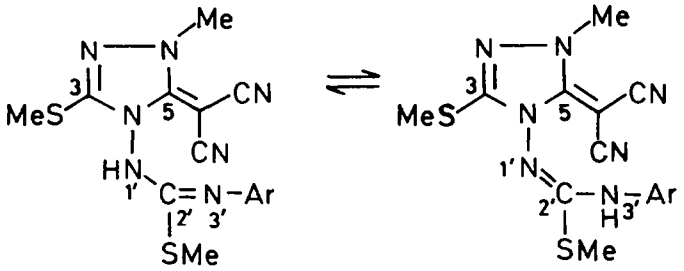
The spectra of the cyanamines (4) are gathered in Table 2.

Table 2. Carbon-13 chemical shifts of cyanamides (4).

Compound	C_3	C_5	N_1-CH_3	C_3-SMe	CN	C_i	C_o	C_m	C_p
4a	159.4	145.8	35.7	13.6	108.8	137.5	118.5	130.3	126.7
4b	159.1	145.2	35.7	13.5	108.3	136.1	120.2	129.9	130.7
4c	159.2	146.2	35.7	13.6	109.1	135.1	119.0	130.7	136.5[a]
4d	159.4	145.4	35.7	13.6	108.3	136.8	120.6	133.0	118.9

[a] C_1-Me: 20.3

The enamines **(5)** show in carbon-13 n.m.r. a splitting of C_5 and C_2' signals attributable to a syn-anti isomerism around the N_1,-C_2, or the C_2,-N_3, bond. It is not possible to determine which bond is involved, i.e., where the tautomeric proton lies, on N_1, or on N_3,.



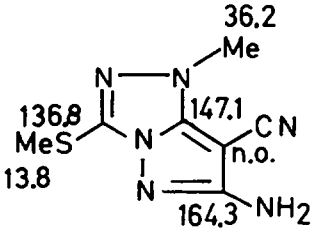
(5) **(5')**

Table 3. Carbon-13 chemical shifts of enamines (5).

Compound	C_3	C_5	N_1-CH_3	C_3-SMe	C_5-C	CN	CN	C_2,	C_2,-SMe	C_i	C_o	C_m	C_p
(5a)	136.6	149.3 149.0	37.8	13.1*	122.9	117.7	117.8	170.7 170.6	13.3*	138.4	127.0	129.0	128.5
(5b)	135.6	149.2 148.8	37.8	13.1*	124.4	117.6	117.8	170.9 170.6	13.4*	137.3	128.6	129.1	131.9
(5c)	135.8	149.3 148.3	37.8	13.1*	123.1	117.7	117.9	170.8 170.6	13.4*	134.0	127.0	129.5	137.1[a]

[a] C_p-Me: 20.6; * These assignments can be reversed.

Finally, the pyrazolotriazole **(6)** chemical shifts were assigned by analogy with other derivatives of the same ring system[10]:



(6)

EXPERIMENTAL

All melting points were determined using a Kofler hot-stage microscope and are uncorrected, i.r. spectra were recorded with a Nicolet FT 5DX spectrometer. ^{1}H-n.m.r. spectra were recorded at 60 MHz on a Varian EM-360A spectrometer using tetramethylsilane as internal standard; in some cases, drops of TFA were added to improve the solubility of the samples which were insolubles in the common solvents. ^{13}C-n.m.r. spectra were recorded on a Bruker WP-80SY spectrometer, with ^{1}H noise decoupling, at 20.15 MHz by the PFT technique. All spectra were measured in DMSO-d_6 solutions, with tetramethylsilane as internal reference in 5 mm tubes. An Aspect 2000 Data System with a 16K memory was used. The pulse conditions were as follows: pulse width, 1.6 μs; acquisition time, 1.82 s; relaxation delay, 0 s; spectral width, 4.5 KHz. Mass spectra (70 eV) were obtained using a Hewlett-Packard 5993C instrument.Combustion analyses were performed with a Perkin-Elmer 240C instrument.

General Procedure for the Preparation of Anhydro 7-aryl-1-methyl-3-methylthio-6-mercapto-1,2,4-triazolo[4,3-b]-1,2,4-triazole Hydroxides(2).

To a well-stirred solution of 4-amino-3,5-bis(methylthio)-1,2,4-triazolium iodide (1.90 g, 6 mmol) in dry dimethylformamide (25 ml), the appropriate aryl isothiocyanate (6 mmol) and triethylamine (12 mmol) were added. The reaction mixture was irradiated with ultrasound at room temperature for 6 h, then it was poured into ice-water (30 ml), and the precipitated solid was filtered off, dried and recrystallised from MeOH/CH_2Cl_2 (1:1). The following derivatives were obtained:

(2a) 7-Phenyl (70%), m.p.145ºC (needles). (Found: C 47.53; H 4.08; N 25.05; S 23.28. $C_{11}H_{11}N_5S_2$ requires: C 47.63; H 4.00; N 25.25; S 23.12.) i.r. (Nujol): 1670,1530, 1455, 1365, 1160, 1125, 910, 838, 753 and 696 cm^{-1}; δ(DMSO-d_6): 2.7 (s,3H), 3.4 (s,3H), 7.6 (s;5H); m/z(%): 245 (100), 212 (21), 161 (13), 144 (18), 128 (97), 118 (38), 104 (13), 91 (12), 77 (59), 69 (25), 57 (39), 43 (34).

(2b) 7-p-Chlorophenyl (72%), m.p.160ºC (needles). (Found: C 42.25; H 3.29; N 22.53; S 20.47. $C_{11}H_{10}ClN_5S_2$ requires: C 42.37; H 3.23; N 22.46; S 20.56). i.r. (Nujol): 1675, 1522, 1365, 1155, 1130, 1087, 1013, 915 and 809 cm^{-1}; δ($CDCl_3$/TFA): 2.8 (s,3H), 3,7 (s, 3H), 7.8 (s,4H); m/z (%):279 (83), 246 (20), 152 (36), 128 (100), 111 (36), 102 (17), 99 (20), 82 (22), 76 (33), 69 (22), 57 (56), 43 (47).

(2c) 7-p-methylphenyl (78%), m.p.157ºC (needles). (Found: C 49.31; H 4.58; N 23.95; S 21.93. $C_{12}H_{13}N_5S_2$ requires: C 49.46; H 4.50; N 24.03; S 22.00). i.r. (Nujol): 1670, 1530, 1365, 1155, 1132 and 850 cm^{-1}; δ($CDCl_3$/TFA): 2.5 (s,3H, 2.7 (s,3H), 3.6 (s,3H), 7.5 (s,4H); m/z (%): 259 (100), 226 (18), 158 (16), 132 (43), 128 (74), 91 (29), 77 (13), 69 (12), 57 (29), 43 (30).

(2d) 7-p-bromophenyl (75%), m.p.163ºC (needles). (Found: C 36.95; H 2.87; N 19.54; S 17.91. $C_{11}H_{10}N_5BrS_2$ requires: C 37.09; H 2.83; N 19.66; S 18.00). i.r. (Nujol): 1660, 1523, 1365, 1166, 1115, 1065, 1007, 910, 809, 695 and 645 cm^{-1}; δ($CDCl_3$/TFA): 2.75 (s,3H), 3.7 (s,3H), 7.65 (d,2H), 8.15 (d,2H); m/z (%) 325 (27), 323 (26), 198 (20), 196 (23), 171 (11), 157 (26), 155 (26), 143 (10), 128 (100), 102 (32), 90 (15), 82 (34), 76 (41), 75 (43), 57 (96), 43 (93).

General Procedure for the Preparation of 7-Aryl-1-methyl-3,6-bis(methylthio)1.2.4-triazolo[4,3-b]-1,2,4-triazolium iodide (3).

To a solution of the 1,2,4-triazolo[4,3-b]1,2,4-trizole **(2)** (1 mmol) in dry benzene (25 ml), methyl iodide (2 mmol) was added. The reaction mixture was stirred at room temperature for 24 h. The precipitated solid was collected by filtration and recrystallised from n-hexane/CH_2Cl_2 (1:1). The following derivatives were obtained:

(3a) 7-phenyl (78%), m.p.155ºC (white prisms). (Found: C 34.41; H 3.48; N 16.64. $C_{12}H_{14}N_5IS_2$ requires: C 34.37; H 3.37; N 16.70). i.r.(Nujol): 1676, 1535, 1381, 1308, 1229, 1172, 1019, 753 and 690 cm^{-1}; $\delta(CDCl_3)$: 2.7 (s,3H), 2.8 (s,3H), 3.75 (s,3H), 7.65 (s,5H); m/z (%): 277 (2), 245 (87), 212 (15), 142 (100), 128 (44), 127 (62), 118 (31), 91 (16), 77 (62), 57 (47), 43 (46).

(3b) 7-p-chorophenyl (80%), m.p. 175ºC (white prisms). (Found: C 31.86; H 2.74; N 15.63. $C_{12}H_{13}N_5ClIS_2$ requires: C 31.76; H 2.89; N 15.43. i.r. (Nujol): 1674, 1536, 1408, 1343, 1366, 1225, 1172, 1093, 1012, 927, 806, 690 and 651 cm^{-1}; $\delta(CDCl_3)$: 2.75 (s,3H), 2.85 (s,3H), 3.8(s,3H), 8.3(d,2H), 7.7 (d,2H); m/z (%): 279 (100), 246 (19), 152 (23), 142 (86), 128 (34), 127 (45), 111 (25), 57 (47), 43 (40).

(3c) 7-p-methylphenyl (77%), m.p.165ºC (white prims). (Found: C 35.91; H 3.84; N 16.24. $C_{13}H_{16}N_5IS_2$ requires: C 36.03; H 3.72, N 16.16). i.r.(Nujol): 1675, 1535, 1382, 1310, 1225, 1175, 1080, 1013, 925, 805 and 690 cm^{-1}; $\delta(CDCl_3)$: 2.45 (s,3H), 2.7 (s,3H), 2.85 (s,3H), 3.7 (s,3H), 7.5 (d,2H), 8.1 (d,2H); m/z (%): 259 (100), 226(14), 158 (11), 142 (95), 132 (30), 128 (50), 127 (51), 105 (15), 77 (17), 65 (28), 57 (35), 43 (35).

(3d) 7-p-bromophenyl (81%), m.p.210ºC (white prisms). (Found: C 29.03; H 2.54; N 13.98. $C_{12}H_{13}N_5BrIS_2$ requires: C 28.93; H 2.63; N 14.06. i.r.(Nujol): 1670, 1535, 1382, 1313, 1223, 1172, 1070, 1013, 804 and 690 cm^{-1}; $\delta(CDCl_3)$: 2.8 (s,3H), 3.8 (s,3H), 7.7-8.2 (m 4H); m/z (%): 325 (27), 323 (27), 142 (65), 128 (34), 127 (54), 76 (18), 64 (24), 57 (34), 43 (42).

Thermolysis of mesoionic compounds (2).

Method A.- The mesoionic compounds **(2)** (1 mmol) was heated under nitrogen at temperature slightly above its melting point for 20-30 minutes. After cooling the solid residue was dissolved in hot ethanol (20 ml) and the resultant solution treated with animal charcoal and concentrated to give a solid which recrystallised from EtOH/ether (1:1) gave **(4)**.

Method B.- Mesoionic compound **(2)** (1 mmol) was suspended in benzene (30 ml). The mixture was stirred at reflux temperature for 3 h. After cooling the solvent was removed under reduced pressure and the solid residue was crystallised from EtOH/ether (1:1) to give 1-methyl-3-methylthio-5-arylcyanamino-1,2,4-triazoles **(4)**. The following derivatives were obtained:

(4a) Ar=C_6H_5 (69%), m.p.70ºC. (Found: C 53.75; H 4.72; N 28.39. $C_{11}H_{11}N_5S$ requires: C 53.86; H 4.52; N 28.55). i.r.(Nujol): 2243, 1597, 1535, 1495, 1291, 1251,753, 736, 690 and 668 cm^{-1}; $\delta(CDCL_3)$: 2.65 (s,3H), 3.85 (s,3H), 7.4-7.6 (m,)H); m/z (%): 245 (M^+,100), 212 (17), 128 (19), 118 (22), 82 (12), 77 (37), 69 (13), 57 (29), 51 (22), 43 (29), 15 (18).

(4b) Ar=4-Cl.C_6H_4 (78%), m.p.122ºC. (Found: C 47.10; H 3.69; N 24.91. $C_{11}H_{10}N_5ClS$ requires: C 47.23; H 3.60; N 25.03). i.r.(Nujol): 2248, 1530, 1495, 1375, 1295, 1257, 1093, 1008 and 832 cm^{-1}; $\delta(CDCl_3)$: 2.6 (s,3H), 3.8 (s,3H), 7.1-7.6 (m,4H); m/z (%): 279 (M^+,100), 246 (22), 195 (9), 177 (8), 152 (36), 128 (84), 125 (10), 111 (31), 102 (15), 75 (32), 69 (19), 57 (50), 43 (41), 15 (24).

(4c) Ar=4-H_3C.C_6H_4 (72%), m.p.87ºC. (Found: C 55.69; H 5.19; N 26.89. $C_{12}H_{13}N_5S$ requires: C 55.58; H 5.05; N 27.01). i.r.(Nujol): 2248, 1535, 1512, 1415, 1381, 1297, 1257, 815 and 730 cm^{-1}; $\delta(CDCl_3)$: 2.40 (s,3H), 2.65 (s,3H), 3.85 (s,3H),7.4 (d,2H), 8.0 (d,2H); m/z (%): 259 (M^+,100), 226 (12), 175 (5), 158 (8), 132 (22), 128 (20), 102 (5), 91 (21), 69 (15), 57 (21), 43 (22), 15 (13).

(4d) Ar=4-Br.C_6H_4 (78%), m.p.124ºC (Found: C 40.65; H 2.99; N 24.76. $C_{11}H_{10}N_5BrS$ requires: C 40.75; H 3.11; N 24.65). i.r.(Nujol): 2248, 1535, 1512, 1297, 1257 and 815 cm^{-1}; δ ($CDCl_3$): 2.6 (s,3H), 3.8 (s,3H), 7.6-8.1 (m,4H); m/z (%): 325 (34), 323 (34), 259 (65), 226 (10), 157 (17), 132 (25), 128 (66), 102 (22), 91 (33), 82 (27) 76 (26), 65 (30), 43 (100), 39 (23), 15 (99).

Similar results can be achieved using 7-aryl-1-methyl-3,6-bis(methylthio)1,2,4-triazolo[4,3-b]-1,2,4-triazolium iodides **(3)**.

Reaction of 7-Aryl-1-methyl-3,6-bis(methylthio)-1,2,4-triazolo[4,3-b]-1,2,4-triazolium Iodides (3) with Malononitrile.

To a well stirred solution of malononitrile (0.132 g, 2 mmol), potassium fluoride (0.35 g, 6 mmol), benzyltriethylammonium chloride (1.36 g, 6 mmol) in dichloromethane (25 ml), a solution of the appropriate 1,2,4-triazolo[4,3-b]-1,2,4-triazolium iodide **(3)** (2 mmol) in dichloromethane (15 ml) was added. The reaction mixture was stirred at room temperature for 24 h. The salts were separated by filtration and the filtrate concentrated to dryness to afford a crude product which recrystallised from EtOH/ethyl acetate gave the enamines **(5)**. The following derivatives were obtained:

(5a) Ar=C_6H_5 (65%), m.p.213ºC. (Found: C 50.29; H 4.37; N 27.41. $C_{15}H_{15}N_7S_2$ requires: C 50.40; H 4.23; N 27.43). i.r.(Nujol): 3194, 2203, 2174, 1568, 1546, 1500, 1376, 1296, 928, 843, 753 and 696 cm^{-1}; δ ($CDCl_3$/TFA): 2.6 (s,6H), 3.9 (s,3H), 7.3-7.7 (m,5H); m/z (%): 357 (M^+,97), 342 (24), 310 (14), 240 (25), 234 (22), 208 (17), 193 (35), 165 (100), 150 (49), 118 (84), 91 (14), 77 (12).

(5b) Ar=4-Cl.C_6H_4 (61%), m.p.196ºC. (Found: C 46.13; H 3.45; N 24.91. $C_{15}H_{14}N_7ClS_2$ requires: C 45.97; H 3.60; N 25.02). i.r.(Nujol): 3177, 2202, 2169, 1568, 1500, 1376, 1347, 1325, 1292, 1093, 1019, 923, 849, 832, 775, 730 and 679 cm^{-1}; δ ($CDCl_3$/TFA): 2.6 (s,3H), 3.9 (s,3H), 7.4 (s,4H); m/z (%): 393 (M^++2,40), 391 (M^+,100), 376 (22), 240 (23), 225 (18), 199 (16), 193 (12), 184 (10), 152 (28).

(5c) Ar=4-H_3C.C_6H_4 (68%), m.p.219ºC. (Found: C 51.59; H 4.46; N 26.51. $C_{16}H_{17}N_7S_2$ requires: C 51.73; H 4.61; N 26.39) i.r.(Nujol): 3200,2203, 2169, 1568, 1546, 1506, 1348, 1325, 1296, 1110, 1019, 974, 923, 843, 821, 804, 741 and 673 cm^{-1}; δ ($CDCl_3$/TFA): 2.35 (s,3H), 2.65 (s,3H), 3.9 (s,3H), 7.6-8.0 (m,4H); m/z (%): 371 (M^+,85), 356 (29), 324 (11), 239 (30), 225 (16), 193 (29), 179 (98), 178 (71), 164 (38), 132 (100), 131 (61), 91 (18).

6-Amino-7-cyano-1-methyl-3-methylthio-pyrazolo[5,1-c]-1,2,4-triazole (6).

To a solution of 1,2,4-triazole **(5)** (2 mmol) in ethanol (25 ml), 1N hydrochloric acid (0.5 ml) was added. The resultant solution was refluxed for 1 h. After cooling the solvent was removed under reduced pressure and the residue was recrystallised from methanol to give **(6)** in 75% yield as colourles needles, m.p.276ºC (lit[9]. m.p. 275-276ºC).

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