New Heterocyclization Reactions for the Preparation of Fused [1,2,4]Triazoles: Synthesis of 1,2,4-Triazolo[4,3-*b*][1,2,4]triazole Derivatives from 4-Amino-1,2,4-triazoles and Carbodi-imides or *via* Iminophosphoranes and Disubstituted Thioureas

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A number of 1,2,4-triazolo[4,3-*b*][1,2,4]triazole derivatives have been prepared. 4-Amino-2-methyl-5-methylthio-2*H*-1,2,4-triazol-3(4*H*)-one (**1**) reacts with diarylcarbodi-imides to yield the corresponding 4-(*N,N'*-diaryl)guanidino-2-methyl-5-methylthio-2*H*-1,2,4-triazol-3(4*H*)-ones (**3**)—(**6**). Reaction of the 2-methyl-5-methylthio-4-triphenylphosphoranylideneamino-2*H*-1,2,4-triazole-3(4*H*)-thione (**2**) with *N,N'*-diaryl thioureas leads to the corresponding 4-(*N,N'*-diaryl)guanidino-2-methyl-5-methylthio-2*H*-1,2,4-triazole-3(4*H*)-thiones (**7**)–(**10**). Compounds (**3**)—(**10**) undergo base-catalysed cyclization to give the 1,2,4-triazolo[4,3-*b*][1,2,4]triazoles (**11**)—(**18**). Sequential treatment of triazolo-triazoles (**15**)—(**18**) with methyl trifluoromethanesulphonate and triethylamine leads to the conjugated mesomeric betaines (**23**)—(**26**); on the other hand, sequential treatment of triazoles (**7**) and (**10**) with methyl trifluoromethanesulphonate and triethylamine leads to the mesomeric betaines (**29**) and (**30**).

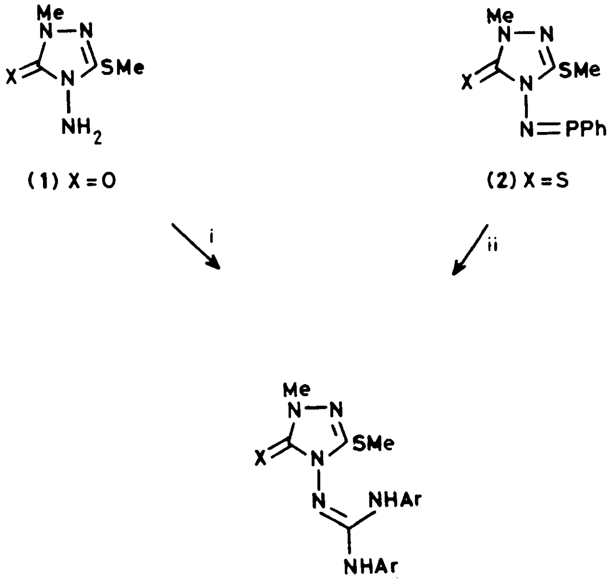
In spite of much work on the synthesis of the 1,2,4-triazolo-[4,3-*b*][1,2,4]triazole ring system, no generally useful procedure for the preparation of 1*H*-derivatives has hitherto been reported.[1–3] We have recently reported[4–6] the reaction of several 4-amino-1,2,4-triazoles with nitriles under basic conditions to give 6-aryl-1-methyl-1,2,4-triazolo[4,3-*b*][1,2,4]triazoles in good yields. Similarly, from the reaction of 4-amino-1-methyl-1,2,4-triazolium cations with aromatic isothiocyanates in the presence of triethylamine,[7] mesoionic compounds derived from the 1,2,4-triazolo[4,3-*b*][1,2,4]triazole ring system are obtained. We report here a convenient preparation of different 1,2,4-triazolo[4,3-*b*][1,2,4]triazoles which display either neutral or mesoionic character. Our approach is based on the cyclization of the appropriate 4-guanidino-1,2,4-triazole derivative to an electrophilic carbon atom of the preformed 1,2,4-triazole ring to give the fused 1,2,4-triazolo[4,3-*b*][1,2,4]triazoles. The 4-guanidino-1,2,4-triazole derivatives are obtained from 4-amino-1,2,4-triazoles by two approaches: (*a*) by reaction with diarylcarbodi-imides and (*b*) by reaction of iminophosphorane derivatives with *N,N'*-diarylthioureas.

Results and Discussion

The *N*-aminoheterocycle (**1**) reacts with diaryl carbodi-imides in dry toluene at reflux temperature for 24 h giving 4-guanidino-1,2,4-triazoles (**3**)—(**6**) as crystalline solids in good yields (53—78%) (Table 1). The i.r. spectra of (**3**)—(**6**) show a strong absorption at 1 682 cm^{-1} due to the carbonyl group. In the ^{1}H n.m.r. spectra the chemical shifts of *S*-methyl and *N*-methyl groups are characteristic at δ 2.55—2.60 and 3.50—3.60 p.p.m., respectively. The mass spectra show the expected molecular ions as the base peaks.

On the other hand, iminophosphorane (**2**), available from 4-amino-2-methyl-5-methylthio-2*H*-1,2,4-triazole-3(4*H*)-thione and triphenylphosphine dibromide, reacts with *N,N*-diaryl thioureas in dry toluene for 24 h to give triphenylphosphine sulphide and the corresponding 4-guanidino-1,2,4-triazoles (**7**)—(**10**) in moderate to good yields (41—85%) (Table 1) (Scheme 1).

The ^{1}H n.m.r. spectra of compounds (**7**)—(**10**) show, amongst others, two singlets at δ 2.53—2.60 and 3.77—3.90 p.p.m. due to the *S*-methyl and *N*-methyl groups, respectively. The mass spectra show the expected molecular ions as the base peaks corresponding to the fragment at *m*/*z* [ArN=C=NAr].



	X	Ar
(**3**)	O	Ph
(**4**)	O	4-ClC$_6$H$_4$
(**5**)	O	4-BrC$_6$H$_4$
(**6**)	O	4-MeOC$_6$H$_4$
(**7**)	S	Ph
(**8**)	S	4-ClC$_6$H$_4$
(**9**)	S	4-BrC$_6$H$_4$
(**10**)	S	4-MeC$_6$H$_4$

Scheme 1. *Reagents:* i, ArN=C=NAr; ii, ArNHCSNHAr

It has been briefly reported[8] that thiocarbohydrazide reacts with two equivalents of diarylcarbodi-imides to yield 5-arylamino-4-(*N,N'*-diarylguanidino)-3-mercapto-1,2,4-triazoles, together with some 4-aryl-3-arylamino-5-mercapto- and 4-aryl-3,5-diarylamino-1,2,4-triazoles.

The 4-guanidino-1,2,4-triazoles (**3**)—(**10**) undergo base-catalysed cyclization by the action of potassium t-butoxide in t-butyl alcohol at reflux temperature for 48 h to give the

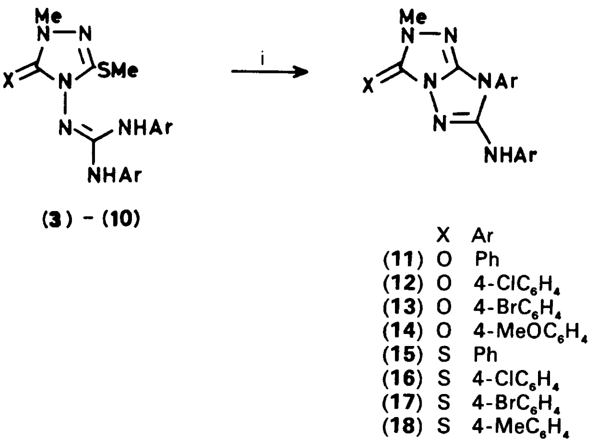
Table 1. 4-(*N*,*N'*-Diaryl)guanidino-1,2,4-triazoles (**3**)—(**10**)

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
(**3**)	White prisms	78	207—209	Toluene	57.5	5.1	23.8	$C_{17}H_{18}N_6OS$	57.61	5.12	23.71
(**4**)	White prisms	69	223—225	Toluene	48.3	3.7	19.8	$C_{17}H_{16}Cl_2N_6OS$	48.23	3.81	19.85
(**5**)	White prisms	53	200—202	Toluene	40.0	3.1	16.5	$C_{17}H_{16}Br_2N_6OS$	39.86	3.15	16.41
(**6**)	White prisms	57	170—172	Toluene	55.1	5.3	20.2	$C_{19}H_{22}N_6O_3S$	55.06	5.35	20.28
(**7**)	White prisms	85	197—199	Toluene	55.1	4.9	22.6	$C_{17}H_{18}N_6S_2$	55.11	4.90	22.68
(**8**)	White prisms	41	192—194	Toluene	46.5	3.7	19.1	$C_{17}H_{16}Cl_2N_6S_2$	46.47	3.67	19.13
(**9**)	White prisms	48	198—200	Toluene	38.5	3.1	15.9	$C_{17}H_{16}Br_2N_6S_2$	38.65	3.05	15.91
(**10**)	White prisms	67	196—198	Toluene	57.1	5.4	21.1	$C_{19}H_{22}N_6S_2$	57.26	5.56	21.09

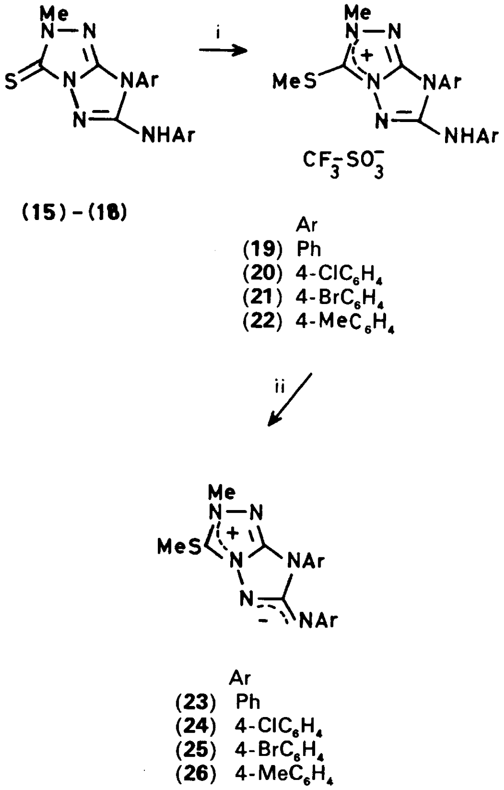
Table 2. 7-Aryl-6-arylamino-2-methyl-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazole-3(2*H*)-ones (**11**)—(**18**)

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
(**11**)	White needles	62	293—295	EtOH	62.7	4.6	27.4	$C_{16}H_{14}N_6O$	62.74	4.61	27.43
(**12**)	White prisms	85	278—280	EtOH	51.3	3.3	22.5	$C_{16}H_{12}Cl_2N_6O$	51.22	3.22	22.40
(**13**)	White plates	87	282—284	EtOH	41.3	2.7	18.2	$C_{16}H_{12}Br_2N_6O$	41.41	2.61	18.11
(**14**)	White plates	50	252—254	EtOH	59.0	5.0	23.0	$C_{18}H_{18}N_6O_3$	59.01	4.95	22.94
(**15**)	White prisms	85	298—300	CH_2Cl_2–ether	59.7	4.3	26.1	$C_{16}H_{14}N_6S$	59.61	4.38	26.07
(**16**)	White prisms	90	287—289	EtOH	49.1	3.1	21.4	$C_{16}H_{12}Cl_2N_6S$	49.12	3.09	21.48
(**17**)	White needles	84	301—303	EtOH	40.1	2.5	17.6	$C_{16}H_{12}Br_2N_6S$	40.02	2.52	17.50
(**18**)	White needles	89	254—256	EtOH	67.9	5.1	23.9	$C_{18}H_{18}N_6S$	67.70	5.18	23.98

corresponding 1,2,4-triazolo[4,3-*b*][1,2,4]triazole derivatives (**11**)—(**18**) as crystalline solids in moderate to excellent yields (50—90%) (Table 2) (Scheme 2). In the ^1H n.m.r. spectra the *N*-methyl group appears as a singlet near to δ 3.50 p.p.m. for compounds (**11**)—(**14**) whereas in the thio analogue series (**15**)—(**18**), it appears near to 3.80 p.p.m.; these values are in good agreement with those previously described[6] for this type of compound. All compounds show the expected molecular ions as the base peak.



Scheme 2. *Reagent:* i, Bu^{t}OK–Bu^{t}OH, heat



Scheme 3. *Reagents:* i, CF_3SO_3Me–CH_2Cl_2, r.t.; ii, Et_3N–DMF, r.t.

Triazolo-triazoles (**15**)—(**18**) undergo *S*-methylation by the action of methyl trifluoromethanesulphonate in dry dichloromethane to give the corresponding triazolo-triazolium salts (**19**)—(**22**) as crystalline solids in good yields (70—85%) (Table 3). When these compounds are treated with triethylamine in dimethylformamide at room temperature they are converted into the corresponding betaines (**23**)—(**26**) in good yields (71—92%) (Table 4) (Scheme 3).

On the other hand, sequential treatment of 4-guanidino-1,2,4-triazoles (**7**) and (**10**) with methyl trifluoromethanesulphonate and triethylamine leads to the betaines (**29**) and (**30**), through the

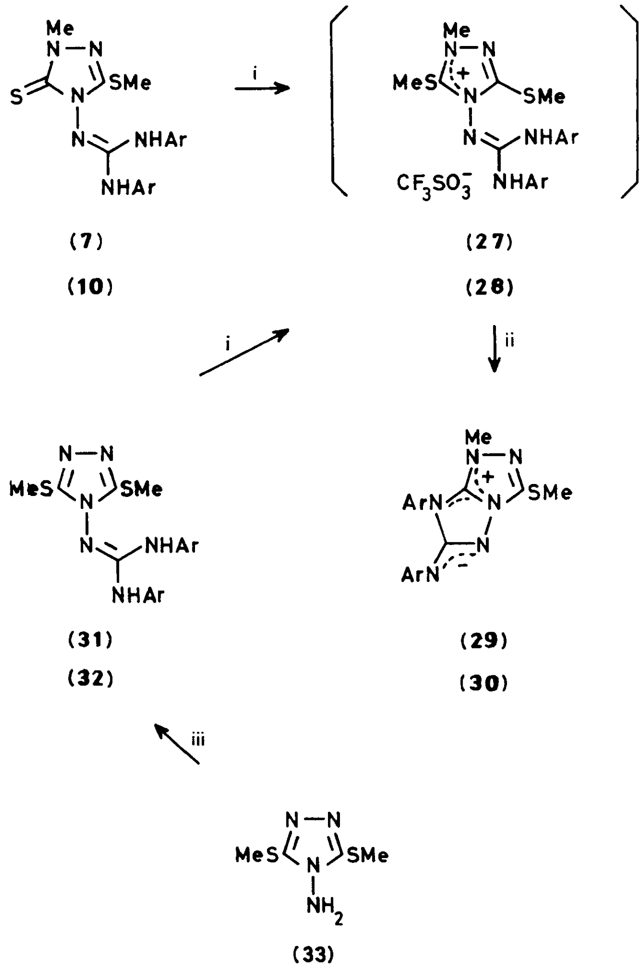
Table 3. 7-Aryl-6-arylamino-2-methyl-3-methylthio-1,2,4-triazolo[4,3-*b*][1,2,4]triazolium trifluoromethanesulphonates (**19**)—(**22**)

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
(**19**)	Colourless plates	85	197—198	CH_2Cl_2	44.5	3.5	17.4	$C_{18}H_{17}F_3N_6O_3S_2$	44.44	3.52	17.27
(**20**)	Colourless prisms	60	205—207	CH_2Cl_2–ether	39.0	2.6	15.0	$C_{18}H_{15}Cl_2F_3N_6O_3S_2$	38.93	2.72	15.13
(**21**)	Colourless prisms	88	242—244	CH_2Cl_2–ether	33.6	2.4	13.0	$C_{18}H_{15}Br_2F_3N_6O_3S_2$	33.56	2.35	13.04
(**22**)	Colourless plates	71	203—205	CH_2Cl_2–ether	46.8	4.1	16.4	$C_{20}H_{21}F_3N_6O_3S_2$	46.68	4.11	16.33

Table 4. 1,2,4-Triazolo[4,3-*b*][1,2,4]triazole betaines (**23**)—(**26**)

Compd.	Crystal form	Yield (%)	M.p. (°C)	Solvent	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
(**23**)	Yellow plates	92	198—200	CH_2Cl_2–ether	60.6	4.9	25.0	$C_{17}H_{16}N_6S$	60.69	4.79	24.98
(**24**)	Yellow needles	82	192—194	CH_2Cl_2–ether	50.3	3.5	20.7	$C_{17}H_{14}Cl_2N_6S$	50.38	3.48	20.73
(**25**)	Yellow needles	91	195—197	CH_2Cl_2–ether	41.3	2.8	17.1	$C_{17}H_{14}Br_2N_6S$	41.32	2.85	17.00
(**26**)	Orange plates	71	202—204	CH_2Cl_2–ether	62.6	5.5	23.2	$C_{19}H_{20}N_6S$	62.61	5.53	23.06

quaternary salts (**27**) and (**28**), respectively. An alternative route to betaines (**29**) and (**30**) is based on the reaction of 4-amino-3,5-bis(methylthio)-1,2,4-triazole (**33**) with diarylcarbodi-imides to give the 4-guanidino-3,5-bis(methylthio)-1,2,4-triazoles (**31**) and (**32**) in good yields (Scheme 4). Sequential treatment of these compounds with methyl trifluoromethanesulphonate and triethylamine leads to compounds (**29**) and (**30**).



Scheme 4. *Reagents:* i, CF_3SO_3Me–CH_2Cl_2/r.t.; ii, Et_3N–DMF/r.t., iii, ArN=C=NAr. In compounds (**7**), (**27**), (**29**), and (**31**), Ar = Ph and in compounds (**10**), (**28**), (**30**), and (**32**), Ar = 4-MeC_6H_4

In accordance with Ollis,[9] compounds (**23**)—(**26**) and (**29**) and (**30**) can be classified as conjugated mesomeric betaines isoconjugated with odd non-alternant hydrocarbon trianions.

Chemical-ionization mass spectra of compounds (**23**)—(**26**) and (**29**) and (**30**) show the expected molecular ion peak as the base peak. In addition, in compounds (**29**) and (**30**) peaks are also found at m/z [ArN=C=NAr], [M^+ − ArNCN], and [ArNCNH].

In the ^1H n.m.r. spectra of compounds (**23**)—(**26**), the chemical shifts of *N*-methyl and *S*-methyl groups are characteristic[6] at δ 3.85—3.95 and 2.75—2.80 p.p.m., respectively. Moreover, for compound (**25**) one 4-chlorophenyl group appears as a singlet which is characteristic of an out-of-plane aryl whereas the other one appears as a multiplet. The *N*-methyl and *S*-methyl groups in the ^1H n.m.r. spectra of compounds (**29**) and (**30**) appear at δ 3.27—3.37 and 2.70 p.p.m., respectively; these values are in good agreement with the reported values[7] for similar compounds.

Experimental

M.p.s were determined with a Kofler hot-stage microscope. Spectral characterizations were performed with the following instruments: i.r., Nicolet FT-5DX; ^1H n.m.r., Varian FT-80 ($SiMe_4$ internal reference; all chemical shifts expressed as δ values); mass spectra (70 eV) Hewlett-Packard 5993C. Combustion analyses were performed with a Perkin-Elmer 240C instrument.

Reagents. All solvents were dried according to standard procedures, distilled and stored over activated molecular sieves 4 Å. 4-Amino-2-methyl-5-methylthio-2*H*-1,2,4-triazol-3(4*H*)-one[6] (**1**), 2-methyl-5-methylthio-4-(triphenylphosphoranylideneamino)-2*H*-1,2,4-triazole-3(4*H*)-thione[10] (**2**), and 4-amino-3,5-bis(methylthio)-1,2,4-triazole[11] (**33**) were prepared following literature methods.

4-(N,N′-*Diaryl*)*guanidino*-1,2,4-*triazoles* (**3**)—(**10**).—(*a*) *From* 4-*amino*-2-*methyl*-5-*methylthio*-2H-1,2,4-*triazol*-3(4H)-*one* (**1**) *and diarylcarbodi-imides.* The appropriate diarylcarbodi-imide (0.01 mol) was added to a solution of compound (**1**) (1.6 g, 0.01 mol) in dry toluene (60 ml). The reaction mixture was stirred at reflux for 24 h and then cooled. The white solid which separated from the solution was collected by filtration, dried, and crystallized from toluene to give the corresponding 4-(N,N′-

*diaryl)guanidino-2-methyl-5-methylthio-2*H*-1,2,4-triazol-3(4*H*)-ones* (**3**)—(**6**) as a crystalline solid.

The following compounds were obtained (yields, m.p.s, and analyses are given in Table 1): N,N′-*Diphenyl derivative* (**3**) $\nu_{max.}$(Nujol) 3 313, 1 682, 1 631, 1 602, 1 546, 1 512, 1 501, 1 450, 1 421, 1 399, 1 348, 1 302, 1 263, 1 240, 1 229, 1 178, 1 076, 1 008, 758, 725, 696, 662, and 628 cm^{-1}; δ_H(CDCl$_3$) 8.85 (1 H, s), 7.7—7.2 (10 H, m), 6.20 (1 H, s), 3.60 (3 H, s), and 2.60 (3 H, s); *m*/*z* (%) 355 (13), 354 (M^+, 57), 307 (12), 195 (100), 194 (93), 160 (17), 144 (11), 118 (10), 102 (26), 93 (36), 92 (39), 91 (12), 77 (37), 65 (39), and 43 (31). N,N′-*Bis*(4-*chlorophenyl*) *derivative* (**4**) $\nu_{max.}$(Nujol) 3 347, 1 682, 1 631, 1 597, 1 585, 1 506, 1 489, 1 415, 1 398, 1 382, 1 348, 1 093, 1 007, 832, 814, and 730 cm^{-1}; δ_H(CDCl$_3$) 8.90 (1 H, s), 7.6—7.0 (8 H, m), 6.40 (1 H, s), 3.50 (3 H, s), and 2.60 (3 H, s); *m*/*z* (%) 426 (M + 4, 15), 425 (16), 424 (M + 2, 72), 423 (22), 422 (M^+, 100), 375 (11), 266 (10), 265 (24), 264 (39), 263 (36), 262 (51), 160 (47), 144 (10), 127 (41), 126 (18), 125 (6), 111 (9), 102 (17), 92 (28), and 43 (17). N,N′-*Bis*(4-*bromophenyl*) *derivative* (**5**) $\nu_{max.}$(Nujol) 3 324, 1 682, 1 631, 1 591, 1 529, 1 512, 1 489, 1 393, 1 347, 1 076, 1 008, 821, and 724 cm^{-1}; δ_H(CDCl$_3$) 8.85 (1 H, s), 7.8—6.8 (8 H, m), 6.50 (1 H, s), 3.50 (3 H, s), and 2.55 (3 H, s); *m*/*z* (%) 514 (M + 4, 55), 513 (22), 512 (M + 2, 100), 511 (12), 510 (M^+, 50), 465 (10), 355 (13), 354 (31), 353 (26), 352 (56), 350 (29), 173 (18), 171 (21), 160 (42), 102 (19), 91 (10), and 43 (7). N,N′-*Bis*(4-*methoxyphenyl*) *derivative* (**6**) $\nu_{max.}$(Nujol) 3 224, 1 682, 1 625, 1 597, 1 540, 1 512, 1 353, 1 245, 1 036, 845, 835, 777, and 721 cm^{-1}; δ_H(CDCl$_3$) 8.20 (1 H, s), 7.6—6.8 (8 H, m), 5.95 (1 H, s), 3.85 (6 H, s), 3.50 (3 H, s), and 2.55 (3 H, s); *m*/*z* (%) 414 (M^+, 100), 377 (6), 267 (7), 256 (11), 255 (73), 254 (99), 240 (11), 239 (51), 147 (31), 133 (17), 123 (63), 122 (50), 108 (37), 102 (12), 95 (12), 92 (10), 80 (10), 77 (8), and 43 (12).

(*b*) *From* 2-*methyl*-5-*methylthio*-4-(*triphenylphosphoranylideneamino*)-2H-1,2,4-*triazole*-3(4H)-*thione* (**2**) *and* N,N′-*diaryl thioureas*. The appropriate *N*,*N*′-diaryl thiourea (0.01 mol) was added to a solution of compound (**2**) (4.36 g, 0.01 mol) in dry toluene (200 ml). After 24 h under reflux the reaction mixture was cooled and the solvent was partially removed under reduced pressure. The solid which separated from the solution was collected by filtration, dried, and crystallized from toluene to give the corresponding 4-(*N*,*N*′-diaryl)guanidino-2-methyl-5-methylthio-2*H*-1,2,4-triazole-3(4*H*)-*thione* (**7**)—(**10**) as a crystalline solid.

The following compounds were obtained (yields, m.p.s, and analyses are given in Table 1): N,N′-*Diphenyl derivative* (**7**) $\nu_{max.}$(Nujol) 3 353, 1 619, 1 597, 1 580, 1 523, 1 489, 1 449, 1 347, 1 313, 1 245, 752, 743, 702, and 694 cm^{-1}; δ_H(CDCl$_3$) 8.20 (1 H, s), 7.8—7.1 (10 H, m), 6.40 (1 H, s), 3.90 (3 H, s), and 2.60 (3 H, s); *m*/*z* (%) 371 (21), 370 (M^+, 93), 278 (11), 277 (7), 196 (11), 195 (82), 194 (100), 176 (87), 161 (20), 160 (17), 118 (37), 93 (64), 65 (55), 51 (49), and 45 (10). N,N′-*Bis*(4-*chlorophenyl*) *derivative* (**8**) $\nu_{max.}$(Nujol) 3 313, 1 619, 1 591, 1 574, 1 529, 1 489, 1 461, 1 348, 1 013, 832, 758, and 713 cm^{-1}; δ_H(CDCl$_3$) 8.25 (1 H, s), 7.6—7.1 (8 H, m), 6.50 (1 H, s), 3.80 (3 H, s), and 2.60 (3 H, s); *m*/*z* (%) 442 (M + 4, 9), 440 (M + 2, 61), 439 (M + 1, 15), 438 (M^+, 96), 266 (13), 265 (12), 264 (67), 263 (26), 262 (100), 176 (32), 161 (22), 129 (29), 128 (18), 127 (82), 125 (73), 118 (14), 113 (3), 112 (6), 111 (39), 102 (29), 101 (15), 100 (10), 99 (33), 91 (11), 90 (24), 75 (44), 74 (24), 73 (20), and 63 (23). N,N′-*Bis*(4-*bromophenyl*) *derivative* (**9**) $\nu_{max.}$(Nujol) 3 336, 1 625, 1 591, 1 580, 1 489, 1 348, 1 319, 1 240, 1 076, 1 008, 821, 804, 719, 696, and 668 cm^{-1}; δ_H(CDCl$_3$) 8.30 (1 H, s), 7.7—7.0 (8 H, m), 6.50 (1 H, s), 3.85 (3 H, s), and 2.60 (3 H, s); *m*/*z* (%) 530 (M + 4, 28), 529 (11), 528 (M + 2, 49), 527 (6), 526 (M^+, 29), 483 (5), 358 (8), 356 (10), 355 (17), 354 (57), 353 (26), 352 (100), 351 (14), 350 (49), 192 (10), 176 (43), 161 (19), 160 (8), 118 (7), 102 (11), 92 (11), 91 (10), 90 (16), 76 (10), 75 (10), 65 (11), and 63 (12). N,N′-*Bis*(4-*tolyl*) *derivative* (**10**) $\nu_{max.}$(Nujol) 3 336, 1 619, 1 608, 1 574, 1 529, 1 512, 1 489, 1 455, 1 348, 1 308, 1 240, 1 172, 1 144, 1 104, 996, 889, 820, 812, 789, 775, 738, and 688 cm^{-1}; δ_H(CDCl$_3$) 7.70 (1 H, s), 7.4—7.1 (8 H, m), 7.00 (1 H, s), 3.80 (3 H, s), 2.50 (3 H, s), 2.30 (3 H, s), and 2.25 (3 H, s); *m*/*z* (%) 339 (17), 398 (M^+, 64), 365 (7), 292 (11), 237 (9), 236 (16), 234 (5), 224 (10), 223 (60), 222 (100), 221 (16), 161 (20), 160 (14), 132 (13), 131 (22), 118 (24), 107 (26), 106 (55), 104 (12), 102 (18), 91 (47), 89 (10), 79 (29), 78 (17), 77 (44), 65 (23), 51 (11), and 45 (11).

General Procedure for the Preparation of 7-*Aryl*-6-*arylamino*-2-*methyl*-7H-1,2,4-*triazolo*[4,3-b][1,2,4]*triazol*-3(2H)-*ones* (**11**)—(**14**) *and* -3(2H)-*thiones* (**15**)—(**18**).—Potassium t-butoxide (0.004 mol) was added to a solution of the appropriate triazole (**3**)—(**10**) (0.002 mol) in t-butyl alcohol (30 ml). The reaction mixture was heated under reflux with stirring for 24 h, then cooled, the solvent evaporated off under reduced pressure, and the residual material scratched with cold water (5 ml). The separated solid was collected by filtration, dried, and recrystallized from the appropriate solvent to give the corresponding 1,2,4-*triazolo*[4,3-b][1,2,4]*triazole* (**11**)—(**18**) as a crystalline solid.

The following compounds were obtained (yields, m.p.s, and analyses are given in Table 2): 2-*methyl*-7-*phenyl*-6-*phenylamino*-7H-1,2,4-*triazolo*[4,3-b][1,2,4]*triazol*-3(2H)-*one* (**11**) $\nu_{max.}$(Nujol) 3 353, 1 704, 1 648, 1 608, 1 585, 1 557, 1 495, 1 455, 764, 736, 713, 691, and 668 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 9.35 (1 H, s), 8.0—7.1 (10 H, m), and 3.45 (3 H, s); *m*/*z* (%) 306 (M^+, 100), 236 (6), 235 (19), 220 (21), 194 (6), 180 (8), 145 (10), 129 (10), 118 (26), 104 (10), 92 (5), 91 (10), 77 (15), and 43 (6). 7-(4-*chlorophenyl*)-6-(4-*chlorophenyl*)*amino*-2-*methyltriazolo-triazolone* (**12**) $\nu_{max.}$(Nujol) 3 228, 3 183, 1 693, 1 614, 1 587, 1 576, 1 560, 1 495, 1 460, 1 410, 1 092, 968, 877, 832, 775, and 713 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 9.10 (1 H, s), 8.0—7.3 (8 H, m), and 3.50 (3 H, s); *m*/*z* (%) 378 (M + 4, 13), 377 (13), 376 (M + 2, 72), 375 (21), 374 (M^+, 100), 264 (7), 263 (5), 262 (20), 179 (5), 163 (10), 154 (8), 152 (23), 151 (7), 138 (8), 126 (6), 111 (11), 99 (7), 75 (7), and 43 (9). 7-(4-*Bromophenyl*)-6-(4-*bromophenyl*)*amino*-2-*methyltriazolo-triazolone* (**13**) $\nu_{max.}$(Nujol) 3 234, 1 693, 1 608, 1 587, 1 572, 1 557, 1 508, 1 491, 1 458, 1 404, 1 246, 1 013, 826, 725, and 713 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 9.40 (1 H, s), 8.1—7.3 (8 H, m), and 3.45 (3 H, s); *m*/*z* (%) 466 (M + 4, 54), 465 (37), 464 (M + 2, 100), 463 (13), 462 (M^+, 50), 395 (5), 394 (8), 393 (6), 386 (9), 384 (9), 354 (20), 353 (15), 352 (38), 350 (18), 270 (9), 198 (11), 196 (10), 173 (7), 171 (11), 155 (6), 90 (5), and 43 (8). 7-(4-*Methoxyphenyl*)-6-(4-*methoxyphenyl*)*amino*-2-*methyltriazolo-triazolone* (**14**) $\nu_{max.}$(Nujol) 3 251, 3 157, 3 086, 1 704, 1 653, 1 608, 1 591, 1 551, 1 512, 1 461, 1 302, 1 246, 1 166, 1 030, 826, 792, 713, 656, and 611 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 8.90 (1 H, s), 7.9—6.9 (8 H, m), 3.90 (3 H, s), 3.80 (3 H, s), and 3.40 (3 H, s); *m*/*z* (%) 367 (22), 366 (M^+, 100), 254 (5), 240 (5), 175 (5), 148 (11), 147 (10), 133 (6), 128 (8), 108 (5), and 45 (5). 7-*Phenyl*-6-*phenylamino*-2-*methyltriazolo-triazolethione* (**15**) $\nu_{max.}$(Nujol) 3 279, 1 614, 1 586, 1 552, 1 495, 1 291, 1 183, 957, 838, 753, 719, 685, and 674 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 9.50 (1 H, s), 8.0—7.1 (10 H, m), and 3.80 (3 H, s); *m*/*z* (%) 323 (21), 322 (M^+, 100), 264 (16), 263 (11), 262 (47), 235 (14), 220 (20), 195 (14), 194 (17), 180 (7), 161 (23), 136 (27), 119 (17), 118 (33), 117 (15), 104 (13), 93 (8), 92 (7), and 77 (28). 7-(4-*Chlorophenyl*)-6-(4-*chlorophenyl*)*amino*-2-*methyltriazolo-triazolethione* (**16**) $\nu_{max.}$(Nujol) 3 426, 1 625, 1 557, 1 495, 1 455, 1 285, 1 186, 1 093, 1 013, 951, 826, 725, and 702 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 9.40 (1 H, s), 8.0—7.3 (8 H, m), and 3.80 (3 H, s); *m*/*z* (%) 394 (M + 4, 15), 393 (17), 392 (M + 2, 75), 391 (28), 390 (M^+, 100), 334 (11), 333 (10), 332 (19), 331 (12), 330 (29), 266 (5), 264 (12), 262 (21), 195 (11), 163 (15), 154 (9), 153 (8), 152 (27), 138 (10), 126 (10), 111 (27), 99 (13), 75 (16), and 45 (13). 7-(4-*Bromophenyl*)-6-(4-*bromophenyl*)*amino*-2-*methyltriazolo-triazolethione* (**17**) $\nu_{max.}$(Nujol) 3 324, 1 614, 1 585, 1 545, 1 489, 1 410, 1 285, 1 013, 957, 843, 826, 806, 748, and 706 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 9.60 (1 H, s), 8.6—7.6 (8 H, m), and 3.80 (3 H, s);

m/*z* (%) 482 ($M + 4$, 53), 481 (22), 480 ($M + 2$, 100), 479 (15), 478 (M^+, 49), 422 (19), 421 (12), 420 (24), 418 (11), 352 (19), 350 (8), 198 (10), 196 (10), 157 (9), 155 (8), and 76 (8). *7-(4-Tolyl)-6-(4-tolyl)amino-2-methyltriazolo-triazolethione* (**18**) $\nu_{max.}$(Nujol) 3 381, 1 631, 1 614, 1 546, 1 512, 1 285, 1 246, 1 183, 1 144, 957, 843, 816, 808, 723, 702, and 667 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 8.95 (1 H, s), 7.6—7.0 (8 H, m), 3.65 (3 H, s), 2.40 (3 H, s), and 2.25 (3 H, s); *m*/*z* (%) 350, (M^+, 100), 349 (5), 334 (5), 292 (12), 291 (11), 290 (23), 222 (20), 221 (5), 161 (10), 131 (8), 108 (6), 107 (7), 106 (29), 105 (9), and 91 (9).

General Procedure for the Preparation of 7-*Aryl*-6-*arylamino*-2-*methyl*-3-*methylthio*-1,2,4-*triazolo*[4,3-b][1,2,4]*triazolium Trifluoromethanesulphonates* (**19**)—(**22**).—Methyl trifluoromethanesulphonate (0.39 g, 0.0024 mol) was added to a solution of the appropriate 1,2,4-triazolo[4,3-*b*][1,2,4]triazolethione (**15**)—(**18**) (0.002 mol) in dry dichloromethane (100 ml). The resultant solution was stirred at room temperature for 24 h. The solvent was evaporated under reduced pressure (30 °C; 20 mmHg) and the product recrystallized from the appropriate solvent to give the corresponding 1,2,4-*triazolo*[4,3-b][1,2,4]-*triazolium trifluoromethanesulphonate* (**19**)—(**22**) as a crystalline solid.

The following compounds were obtained (yields, m.p.s, and analyses are given in Table 3): 7-*Phenyl*-6-*phenylamino derivative* (**19**) $\nu_{max.}$(Nujol) 3 256, 1 619, 1 602, 1 580, 1 540, 1 280, 1 257, 1 161, 1 030, 747, 725, 691, and 634 cm^{-1}; δ_H(CDCl$_3$ + TFA) 7.80 (5 H, s), 7.7—7.1 (5 H, m), 4.10 (3 H, s), and 3.00 (3 H, s). 7-(4-*Chlorophenyl*)-6-(4-*chlorophenyl*)*amino derivative* (**20**) $\nu_{max.}$(Nujol) 3 256, 1 625, 1 580, 1 557, 1 489, 1 461, 1 291, 1 251, 1 228, 1 178, 1 155, 1 146, 1 092, 1 030, 845, 829, 808, 752, and 634 cm^{-1}; δ_H(CDCl$_3$ + TFA) 8.1—7.5 (4 H, m), 7.40—7.10 (4 H, m), 4.15 (3 H, s), and 3.10 (3 H, s). 7-(4-*Bromophenyl*)-6-(4-*bromophenyl*)*amino derivative* (**21**) $\nu_{max.}$(Nujol) 3 267, 1 625, 1 580, 1 552, 1 489, 1 461, 1 291, 1 251, 1223, 1 149, 1 030, 843, 826, 804, 747, and 634 cm^{-1}; δ_H(CDCl$_3$ + TFA) 8.0—7.5 (4 H, m), 7.4—7.2 (4 H, m), 4.15 (3 H, s), and 3.00 (3 H, s). 7-(4-*Tolyl*)-6-(4-*tolyl*)*amino derivative* (**22**) $\nu_{max.}$(Nujol) 3 296, 1 648, 1 626, 1 609, 1 582, 1 512, 1 339, 1 279, 1 258, 1 192, 1 157, 1 030, 820, 812, 719, and 634 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 9.60 (1 H, s), 7.5—7.2 (8 H, m), 4.00 (3 H, s), 2.80 (3 H, s), 2.40 (3 H, s), and 2.30 (3 H, s).

General Procedure for the Preparation of Betaines (**23**)—(**26**).—The appropriate 1,2,4-triazolo[4,3-*b*][1,2,4]triazolium trifluoromethanesulphonate (**19**)—(**22**) (0.002 mol) in dry dimethylformamide (8 ml) and triethylamine (0.22 g, 0.0022 mol) were stirred at room temperature for 12 h. The mixture was poured into ice–water (40 ml) and the precipitated solid filtered off and recrystallized from dichloromethane–ether (1 : 1, v/v) to give the corresponding betaines (**23**)—(**26**) as crystalline solids.

The following compounds were obtained (yields, m.p.s, and analyses are given in Table 4: *Compound* (**23**; Ar = Ph) $\nu_{max.}$(Nujol) 1 638, 1 608, 1 558, 1 483, 1 456, 1 327, 1 315, 1 285, 1 167, 1 081, 1 030, 985, 826, 792, 758, 730, 696, and 673 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 8.6—6.9 (10 H, m), 4.00 (3 H, s), and 2.85 (3 H, s); *m*/*z* (%) 336 (M^+, 100), 335 (14), 322 (10), 320 (11), 291 (11), 277 (8), 276 (10), 220 (11), 194 (7), 161 (10), 150 (15), 132 (10), 91 (7), 77 (21), and 43 (14).

Compound (**24**; Ar = 4-ClC$_6$H$_4$) $\nu_{max.}$(Nujol) 1 625, 1 585, 1 568, 1 501, 1 489, 1 331, 1 291, 1 251, 1 161, 1 098, 1 030, 843, 815, and 719 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 8.0—7.5 (4 H, m), 7.4—7.05 (4 H, m), 3.90 (3 H, s), and 2.75 (3 H, s); *m*/*z* (%) 408 ($M + 4$, 13), 407 (17), 406 ($M + 2$, 72), 405 (38), 404 (M^+, 100), 403 (26), 340 (8), 288 (10), 255 (5), 254 (11), 253 (7), 152 (8), 111 (8), and 43 (18).

Compound (**25**; Ar = 4-BrC$_6$H$_4$) $\nu_{max.}$(Nujol) 1 608, 1 563, 1 484, 1 461, 1 325, 1 314, 1 166, 1 070, 1 030, 1 013, 832, 747, and 719 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 8.1—7.6 (4 H, m), 7.25 (4 H, s), 3.90 (3 H, s), and 2.80 (3 H, s); *m*/*z* (%) 496 ($M + 4$, 52), 495 (25), 494 ($M + 2$, 100), 493 (18), 492 (M^+, 47), 480 (8), 354 (10), 352 (17), 350 (8), 325 (50), 324 (10), 323 (48), 300 (57), 299 (25), 298 (58), 297 (17), 241 (14), 157 (16), 155 (15), 84 (15), and 43 (19).

Compound (**26**; Ar = 4-Tolyl) $\nu_{max.}$(Nujol) 1 636, 1 619, 1 585, 1 568, 1 506, 1 314, 1 280, 1 166, 1 109, 1 030, 985, 827, 818, 773, and 719 cm^{-1}; δ_H(CDCl$_3$) 7.80—6.90 (8 H, m), 3.85 (3 H, s), 2.80 (3 H, s), 2.35 (3 H, s), and 2.25 (3 H, s); *m*/*z* (%) 364 (M^+, 100), 363 (30), 350 (13), 319 (10), 234 (10), 233 (8), 164 (11), 146 (7), 132 (10), 91 (14), 77 (7), and 43 (9).

General Procedure for the Preparation of Betaines (**29**).—(**30**).—A solution of the 4-amino-3,5-bis(methylthio)-1,2,4-triazole (0.7 g, 0.004 mol) and the appropriate diarylcarbodi-imide (0.004 mol) in dry toluene was heated at reflux temperature for 60 h while being stirred. After the mixture had cooled, the precipitated solid was collected by filtration, dried, and crystallized from toluene to give the corresponding 4-(*N*,*N*′-diaryl)guanidino-3,5-bis(methylthio)-1,2,4-triazole as a crystalline solid. The following compounds were obtained: 4-(N,N′-*Diphenyl*)*guanidino*-3,5-*bis*(*methylthio*)-1,2,4-*triazole* (**31**) (1.13 g, 77%) as colourless prisms, m.p. 214—216 °C (Found: C, 55.1; H, 4.9; N, 22.6. C$_{17}$H$_{18}$N$_6$S$_2$ requires C, 55.11; H, 4.89; N, 22.68%); $\nu_{max.}$(Nujol) 3 330, 1 608, 1 589, 1 583, 1 537, 1 501, 1 456, 1 450, 1 418, 1 358, 1 294, 1 230, 1 184, 976, 758, 696, and 690 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 8.65 (1 H, s), 8.60 (1 H, s), 7.5—6.9 (10 H, m), and 2.50 (6 H, s); *m*/*z* (%) 370 (M^+, 26), 322 (15), 195 (29), 194 (100), 93 (34), 92 (9), 91 (13), 77 (36), 65 (18), 51 (26), and 45 (25). 4-N,N′-(4-*Tolyl*)*guanidino*-3,5-*bis*(*methylthio*)-1,2,4-*triazole* (**32**) (0.88 g, 63%) as colourless prisms, m.p. 222—224 °C (Found: C, 57.3; H, 5.5; N, 21.0. C$_{19}$H$_{22}$N$_6$S$_2$ requires C, 57.26; H, 5.56; N, 21.08%); $\nu_{max.}$(Nujol) 3 415, 1 608, 1 591, 1 580, 1 514, 1 452, 1 441, 1 391, 1 308, 1 282, 1 244, 1 178, 1 022, 985, 970, 818, 804, 789, 748, and 706 cm^{-1}; δ_H[(CD$_3$)$_2$SO] 8.42 (1 H, s), 8.33 (1 H, s), 7.4—6.8 (8 H, m), 2.50 (6 H, s), and 2.20 (6 H, s); *m*/*z* (%) 398 (M^+, 40), 350 (23), 223 (31), 222 (67), 175 (11), 132 (24), 131 (23), 118 (24), 116 (10), 107 (67), 106 (84), 104 (13), 91 (72), 90 (10), 77 (36), 65 (37), 48 (86), 47 (100), 42 (20), and 45 (64).

Methyl trifluoromethanesulphonate (0.39 g, 0.0024 mol) was added to a solution of the triazole (**31**) or (**32**) (0.002 mol) in dry dichloromethane (25 ml). The mixture was stirred at room temperature for 24 h and concentrated to dryness to afford a crude product which was dissolved in dimethylformamide (15 ml). To the resulting solution was added triethylamine (0.40 g, 0.004 mol) and the mixture was stirred at room temperature for 24 h. The reaction mixture was poured into ice-water (50 ml) and the solid precipitated was collected by filtration, dried, and recrystallized from dichloromethane–ether (1 : 1, v/v) to give the corresponding betaine (**29**)—(**30**).

Compound (**29**; Ar = Ph) (0.49 g, 53%) as colourless prisms, m.p. 187—188 °C (Found: C, 60.6; H, 4.8; N, 24.9. C$_{17}$H$_{16}$N$_6$S requires C, 60.67; H, 4.79; N, 24.97%); $\nu_{max.}$(Nujol) 1 670, 1 610, 1 574, 1 558, 1 508, 1 456, 1 344, 1 271, 1 157, 1 016, 987, 897, 760, and 690 cm^{-1}; δ_H(CDCl$_3$) 7.6—6.7 (10 H, m), 3.27 (3 H, s), and 2.70 (3 H, s); *m*/*z* (%) 336 (M^+, 100), 335 (16), 260 (28), 220 (23), 219 (8), 195 (11), 194 (67), 193 (10), 118 (31), 91 (21), 77 (41), and 51 (28).

Compound (**30**; Ar = 4-Tolyl) (0.61 g, 55%) as colourless prisms, m.p. 194—195 °C (Found: C, 62.8; H, 5.5; N, 23.1. C$_{19}$H$_{20}$N$_6$S requires C, 62.61; H, 5.53; N, 23.06); $\nu_{max.}$(Nujol) 1 676, 1 619, 1 585, 1 515, 1 347, 1 217, 1 149, 1 013, 894, 826, 781, and 702 cm^{-1}; δ_H(CDCl$_3$) 7.4—6.9 (8 H, m), 3.37 (3 H, s), 2.70 (3 H, s), 2.39 (3 H, s), and 2.22 (3 H, s); *m*/*z* (%) 364 (M^+, 100), 363 (43), 317 (14), 274 (9), 250 (9), 248 (10), 235 (11), 234 (47), 233 (14), 222 (17), 146 (10), 132 (18), 131 (13), 91 (21), and 77 (8).

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