Synthesis, Molecular Structure, and Reactions of 1*H*-1,2,4-Triazolo[4,3-*a*]pyrimidinium Betaines

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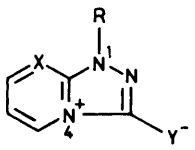
Novel 1-substituted 1,2,4-triazolo[4,3-*a*]pyrimidinium betaines have been prepared and characterised. Treatment of 1-alkyl-1-(4,6-dimethylpyrimidin-2-yl)hydrazines (**2f**—**j**) with phosgene gave a series of 1,2,4-triazolo[4,3-*a*]pyrimidinium chlorides (**3a**—**e**) which were subsequently converted by ammonia into 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olates (**5a**—**e**). Analogous 3-thiolates (**5g**—**k**) were best synthesized by treating the appropriate hydrazines (**2f**—**j**) with carbon disulphide. The 1-(3-hydroxypropyl) derivatives (**5f**) and (**5l**) were obtained by deprotection of benzyl derivatives (**5e**) and (**5k**) using BCl_3 in dichloromethane at −10 °C. Methylation of the 3-thiolate derivative (**5g**) with iodomethane gave the salt (**9**) which was subsequently transformed by methylamine into the triazole derivative (**10**). 1,5,7-Trimethyl-1*H*-1,2,4-triazolo[4,3-*a*]pyrimidinium-3-thiolate gave 5-amino-1-methyl-1*H*-1,2,4-triazole-3-thiol (**11**) on treatment with hydrazine hydrate. The molecular structure of 1-benzyl-5,7-dimethyl-1*H*-1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olate (**5b**) has been determined by *X*-ray crystallography.

Investigations on monocyclic mesoionic compounds[1,2] have been extensive; such heterocycles are interesting from theoretical[3] and structural[4] viewpoints, they are valuable in 1,3-dipolar cycloaddition reactions,[1,2,5] and their potential in medicinal chemistry has been recognised.[6]

Bicyclic heteroaromatic betaines[5] are less common and their scope in heterocyclic synthesis remains incompletely defined.[7] A number of 1,2,4-triazolo[4,3-*a*]pyridinium betaines (**1**; X = CH; Y = O, S) have been prepared[8–14] but there are no reports on analogous 1,2,4-triazolo[4,3-*a*]pyrimidinium betaines (**1**; X = N; Y = O, S). We now describe the synthesis and structural characterisation of a series of -olates (**1**; X = N; Y = O) and -thiolates (**1**; X = N; Y = S) in this ring system and outline briefly one mode of ring fission induced by nucleophiles.



(**1**)

Synthesis.—The 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olates (**5a**—**f**) were prepared by adaptation of a general method[8] developed for the synthesis of analogues in the 1,2,4-triazolo[4,3-*a*]pyridine series and required a number of 1-alkyl-1-(4,6-dimethylpyrimidin-2-yl)hydrazines (**2f**—**j**). 1-(4,6-Dimethylpyrimidin-2-yl)-1-methylhydrazine (**2f**) was prepared[15] by the reaction of 2-chloro-4,6-dimethylpyrimidine with methylhydrazine but a more general method was adopted for synthesis of analogous compounds (**2g**—**j**). Thus alkylation [NaH, RBr, tetrahydrofuran (THF)][16] of the hydrazone (**2a**) followed by acidic hydrolysis (2M-HCl, reflux) gave the hydrazines (**2g**—**j**) in good overall yield.

Treatment of the hydrazines (**2f**—**j**) with phosgene at room temperature gave the pale yellow 1,2,4-triazolo[4,3-*a*]pyrimidinium chlorides (**3a**—**e**) in high yield. Satisfactory microanalysis of the salts (**3**) proved difficult to obtain because of ready dissociation into the respective free bases upon attempted recrystallisation. However, one compound, (**3a**), was obtained analytically pure with data indicating a monohydrochloride salt. The ^{1}H n.m.r. spectra (Table 1) were consistent with the bicyclic structure (**3**) and exhibited the characteristic coupling (*J* 1 Hz) between the 5-methyl substituent and 6-H also observed in the covalent 1,2,4-triazolo[4,3-*a*]pyrimidin-3-one derivative (**4**);* an additional feature is the downfield shift of ^{1}H n.m.r. resonances of the salts (**3**) relative to those of (**4**), which can be attributed to the positive charge associated with the ring system. Representation of the salts (**3**) in the keto tautomeric form in the solid state is supported by an i.r. absorption in the carbonyl (1 685 cm^{-1}) and NH regions (3 150 cm^{-1}).

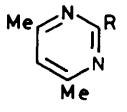
The hydrochloride salts (**3**) were suspended in chloroform and treated with ammonia gas to give the corresponding 1*H*-1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olates (**5a**—**e**) as bright yellow crystalline solids in good yield. The heteroaromatic betaine structure (**5**) is supported by analytical and *X*-ray crystallographic data (see following section). I.r. spectra of the betaines (**5**) show strong absorption in the C=O stretching

Table 1. ^{1}H N.m.r. spectra[a] of hydrochloride salts (**3**)

Compound	7-Me[b]	5-Me[b]	NCH_2R'	6-H
(**3a**)	2.67 (s)	2.90 (d)[c]	3.93 (s)	7.05 (q)[c]
(**3b**)	2.69 (s)	2.93 (d)	5.52 (s)	7.14 (q)
(**3c**)	2.66 (s)	2.93 (d)	4.31 (t)	7.11 (q)
(**3d**)	2.66 (s)	2.91 (d)	4.31 (t)	7.39 (q)

[a] Measured in CD_3OD solution and quoted in p.p.m. from $SiMe_4$. [b] Assignments of chemical shifts for 7-Me and 5-Me were based on (a) values in closely related 1,2,4-triazolo[4,3-*a*]pyrimidines, including quaternary compounds (refs. 21*a*, 21*c*—*e*) and (b) the relatively large downfield shift of 5-Me in passing from the betaine -olate series (**5a**—**f**) to the -thiolate series (**5g**—**l**). [c] *J* 1 Hz.

* Prepared by reaction of 2-hydrazino-4,6-dimethylpyrimidine with phosgene and pyridine in THF. The reported synthesis (see T. Okabe, E. Taniguchi, and K. Maekawa, *Agric. Biol. Chem.*, 1973, **37**, 441) of compound (**4**) by reaction of 5-amino-2-hydroxy-1,2,4-triazole with acetylacetone in refluxing acetic acid is ambiguous and has also been claimed to yield the isomeric 1,2,4-triazolo[1,5-*a*]pyrimidin-2-one [see L. Gsell and W. Meyer, G.P. 2 749 753/1978 (*Chem. Abstr.*, 1978, **89**, 43495v).



(2)

R

a NHN=CHPh

b $N(CH_2Ph)N=CHPh$

c $N(Pr^n)N=CHPh$

d $N(C_5H_{11})N=CHPh$

e $N(CH_2CH_2CH_2OCH_2Ph)N=CHPh$

f $N(Me)NH_2$

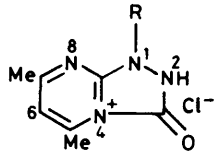
g $N(CH_2Ph)NH_2$

h $N(Pr^n)NH_2$

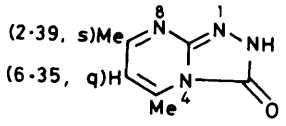
i $N(C_5H_{11})NH_2$

j $N(CH_2CH_2CH_2OCH_2Ph)NH_2$

k N(Me)NHCSNHPh



(3)



(2·39, s)Me

(6·35, q)H

(2·75, d)

(4)

R

a Me

b CH_2Ph

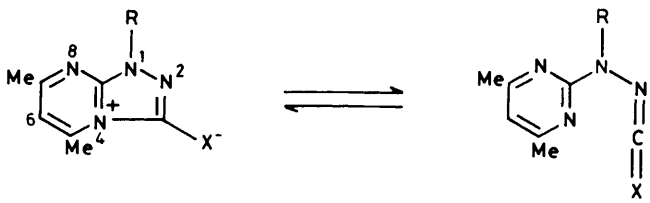
c Pr^n

d C_5H_{11}

e $CH_2CH_2CH_2OCH_2Ph$

region (1 680—1 690 cm^{-1}) close to values observed in mesoionic 1,2,4-triazoles (1 660 cm^{-1}),[17] 1,2,4-triazolo[4,3-*a*]pyridinium betaines (1 660 cm^{-1},[8] and 1,2,4-triazolo[1,5-*a*]pyridinium betaines (1 670 cm^{-1}).[18] The absence of i.r. absorption bands (Nujol mull or in solution in chloroform) characteristic of the isocyanate group (2 250—2 270 cm^{-1}) excludes the possibility of an open-chain structure (**5A**). ^1H N.m.r. spectra of the betaines (Table 2) show the characteristic 5-Me to 6-H coupling (*J* 1 Hz); downfield shifts compared with the model compound (**4**) are less marked than those of the hydrochlorides (**3**) but do indicate a degree of positive charge associated with the ring system.

Three approaches were evaluated for synthesis of 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-thiolates (**5g**—**k**). Thermolysis of the neat thiosemicarbazide (**2k**) (Method A) gave 1,5,7-



(5)

(5A)

	R	X
a	Me	O
b	CH_2Ph	O
c	Pr^n	O
d	$[CH_2]_4Me$	O
e	$[CH_2]_3OCH_2Ph$	O
f	$[CH_2]_3OH$	O
g	Me	S
h	CH_2Ph	S
i	Pr^n	S
j	$[CH_2]_4Me$	S
k	$[CH_2]_3OCH_2Ph$	S
l	$[CH_2]_3OH$	S

trimethyl-1*H*-1,2,4-triazolo[4,3-*a*]pyrimidinium-3-thiolate (**5g**) in 45% yield and this compound was also obtained by treating 4,6-dimethyl-2-(1-methylhydrazino)pyrimidine (**2f**) with thiophosgene (Method B,[8] 54%) or with carbon disulphide (Method C, 83%); related compounds in the thiolate series (**5h**—**k**) were therefore prepared by the higher yielding method C.

The i.r. spectra of the 3-thiolates (**5g**—**k**) showed a C=S stretching frequency at 1 345 cm^{-1} but an absence of absorption in the region 1 990—2 140 cm^{-1} which could have been ascribed to the isothiocyanate group of an open-chain tautomer (**5A**; X = S). ^1H N.m.r. chemical shifts and coupling constants of the thiolates (**5g**—**k**) (Table 3) are similar to those of the oxygen analogues (**5a**—**f**) but downfield shifts are enhanced, particularly of the 5-Me and 6-H protons. A similar trend has been reported[19] for mesoionic *s*-triazolium-olates and -thiolates with the greater deshielding effect of the exocyclic sulphur atom attributed[19] to its diminished electron-releasing mesomeric influence compared with oxygen.[20]

The ^{13}C n.m.r. spectra of 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olates (**5a**—**d**) and 3-thiolates (**5g**—**j**) (Table 4) were interpreted by analysis of spin-coupled spectra and by comparison with model compounds.[21,22] The carbonyl chemical shifts for C-3 in the 3-olate series (**5a**—**d**) show a small downfield shift (*ca.* 3 p.p.m.) compared with that (149.57 p.p.m.) of the covalent 1,2,4-triazolo[4,3-*a*]pyrimidone (**4**), suggesting little polarisation of the C=O bond. The downfield shifts in the 3-thiolate series (**5g**—**j**) relative to the 3-olate series (**5a**—**d**),

Table 2. ^1H N.m.r. spectra[a] of 1*H*-1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olates (**5**)

Compound	7-Me[b]	5-Me[b]	NCH_2R'	6-H
(**5a**)	2.55 (s)	2.90 (d)[c]	3.77 (s)	6.73 (q)[c]
(**5b**)	2.58 (s)	2.87 (d)	5.29 (s)	6.71 (q)
(**5c**)	2.56 (s)	2.90 (d)	4.13 (t)	6.75 (q)
(**5d**)	2.56 (s)	2.90 (d)	4.18 (t)	6.73 (q)

[a] Measured in CD_3OD solution and quoted in p.p.m. from $SiMe_4$. [b] See footnote *b* in Table 1 for comment on assignments. [c] *J* 1 Hz.

Table 3. ^1H N.m.r. spectra[a] of 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-thiolates

Compound	7-Me[b]	5-Me[b]	NCH_2R'	6-H
(**5g**)	2.62 (s)	3.35 (d)[c]	3.90 (s)	6.87 (q)[c]
(**5h**)	2.64 (s)	3.55 (d)	5.42 (s)	6.84 (q)
(**5i**)	2.63 (s)	3.41 (d)	4.26 (q)	6.88 (q)
(**5j**)	2.63 (s)	3.40 (d)	4.28 (q)	6.70 (q)

[a] Measured in CD_3OD solution and quoted in p.p.m. from $SiMe_4$. [b] See footnote *b* in Table 1 for comment on assignments. [c] *J* 1 Hz.

Table 4. ^{13}C N.m.r. spectra[a] of 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olates and -thiolates (**5**)

Compound	C-3	C-5[b]	C-6	C-7[b]	C-8a
(**5a**)	150.01	148.66	112.66	173.73	144.10
(**5b**)	152.94	149.86	111.03	171.40	143.26
(**5c**)	153.07	149.65	110.74	170.97	143.09
(**5d**)	153.05	149.64	110.69	170.92	143.26
(**5g**)	160.57	153.15	114.79	172.94	147.68
(**5h**)	159.38	151.88	113.73	171.65	145.89
(**5i**)	159.41	151.04	113.74	171.47	146.26
(**5j**)	159.16	151.63	113.49	171.23	145.91

[a] Measured at 250 MHz in CD_3OD (**5a**—**d**) and CD_3OD–$CDCl_3$ (5:2) (**5g**—**j**). [b] C-5 and C-7 chemical shifts were assigned from ^{13}C-{^1H}decoupling experiments using knowledge of ^1H n.m.r. resonances of CH_3 groups at C-5 and C-7 (see footnote *b* in Table 1).

Table 5. Derived geometrical parameters for the betaine (**5b**)

(a) Bond lengths (Å) with standard deviations in parentheses

N(1)–N(2)	1.3942(21)	C(3)–C(6)	1.4953(24)
N(1)–C(1)	1.3360(24)	C(4)–C(5)	1.3557(23)
N(2)–C(2)	1.3137(21)	C(5)–C(7)	1.491(3)
N(2)–C(8)	1.4430(24)	C(8)–C(9)	1.509(3)
N(3)–C(2)	1.3450(21)	C(9)–C(10)	1.381(3)
N(3)–C(3)	1.3237(21)	C(9)–C(14)	1.380(3)
N(4)–C(1)	1.4540(22)	C(10)–C(11)	1.383(3)
N(4)–C(2)	1.3641(20)	C(11)–C(12)	1.370(4)
N(4)–C(5)	1.3796(21)	C(12)–C(13)	1.362(4)
O(1)–C(1)	1.2269(23)	C(13)–C(14)	1.387(4)
C(3)–C(4)	1.4148(23)		

(b) Bond angles (degrees) with standard deviations in parentheses

N(2)–N(1)–C(1)	106.38(14)	N(3)–C(3)–C(6)	116.94(14)
N(1)–N(2)–C(2)	112.26(14)	C(4)–C(3)–C(6)	120.48(14)
N(1)–N(2)–C(8)	120.96(14)	C(3)–C(4)–C(5)	121.47(15)
C(2)–N(2)–C(8)	126.72(15)	N(4)–C(5)–C(4)	115.92(14)
C(2)–N(3)–C(3)	114.59(14)	N(4)–C(5)–C(7)	119.40(14)
C(1)–N(4)–C(2)	107.23(13)	C(4)–C(5)–C(7)	124.66(16)
C(1)–N(4)–C(5)	133.23(14)	N(2)–C(8)–C(9)	113.60(15)
C(2)–N(4)–C(5)	119.54(13)	C(8)–C(9)–C(10)	121.23(17)
N(1)–C(1)–N(4)	106.99(15)	C(8)–C(9)–C(14)	120.34(17)
N(1)–C(1)–O(1)	129.63(18)	C(9)–C(10)–C(11)	121.02(19)
N(4)–C(1)–O(1)	123.37(16)	C(10)–C(9)–C(14)	118.38(14)
N(2)–C(2)–N(3)	126.95(15)	C(10)–C(11)–C(12)	119.74(22)
N(2)–C(2)–N(4)	107.14(14)	C(11)–C(12)–C(13)	120.0(3)
N(3)–C(2)–N(4)	125.91(14)	C(12)–C(13)–C(14)	120.5(3)
N(3)–C(3)–C(4)	122.56(15)	C(13)–C(14)–C(9)	120.31(18)

particularly noticeable at C-3, can be attributed to a greater polarisation of the C=S bond; a similar trend has been noted in ^{13}C n.m.r. chemical shifts of sydnones and their anhydro 5-mercapto-1,2,3-oxatriazolium analogues.[23a]

A longer term objective of our work is the synthesis of analogues of purine-based antiviral agents {*e.g.* 9-[2-(hydroxyethoxy)methyl]guanine}.[23b] The protected hydroxyalkyl derivatives (**5e**), (**5k**) were synthesized with this in mind and could be deprotected (BCl_3, CH_2Cl_2, -10 °C) to furnish model compounds (**5f**), (**5l**) in moderate yield.

X-Ray Molecular Structure.—The solution spectral properties and chemical reactivity of mesoionic compounds and their bicyclic congeners can generally be accommodated in terms of a heteroaromatic structure.[2] From i.r. studies it is apparent that there is often considerable bond polarisation in exocyclic C–O, C–S, and CNR groups, and in some mesoionic systems this property is apparent in the solid state (*cf.* relatively long C–O and C–S bond lengths of 1.33 Å and 1.66 Å from *X*-ray analysis

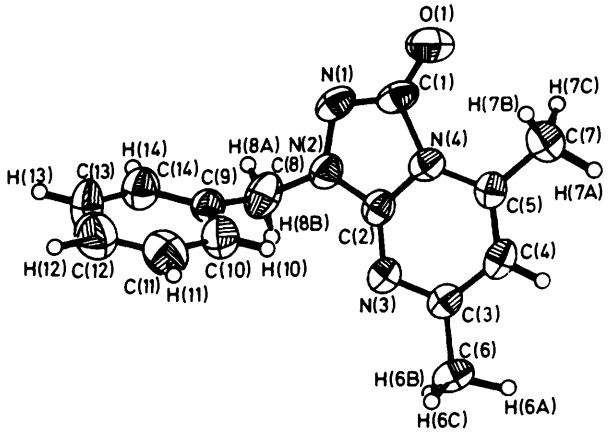


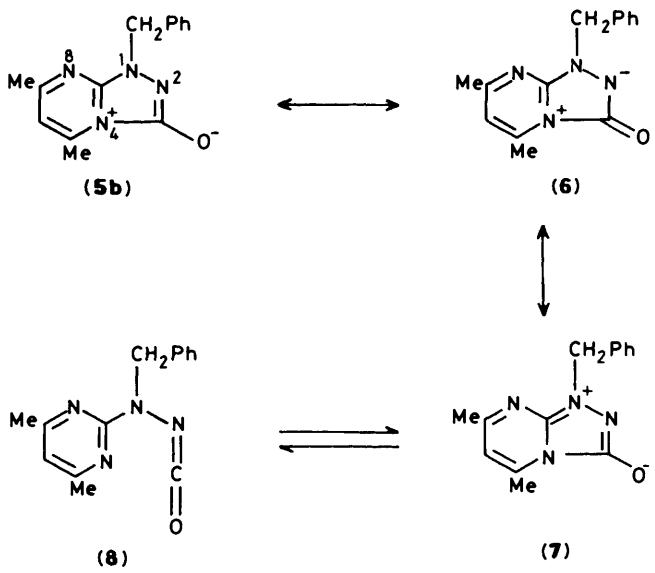
Figure. *X*-Ray molecular structure of the betaine (**5b**) with the crystallographic numbering system. The alternative positions for the hydrogen atoms of the methyl groups at C(6) and C(7) have been omitted for clarity

of 3-amino-2-methylthio-5-phenylthiazolium-4-olate[24] and 1,3-diphenyltetrazolium-5-thiolate[4] respectively). In contrast the exocyclic C–O bond lengths in a series of sydnones[4,25–28] (*e.g.* 1.213 Å in a bis-sydnone[25]) and in 4,5-diphenylisosydnone (1.207 Å)[4] are relatively short (*cf.* values of *ca.* 1.20—1.22 Å in simple carbonyl compounds and 1.21—1.27 Å in amides), and this feature, added to the distortion of the C–C–O (exocyclic) bond angle (*e.g.* θ 135.8° in the bis-sydnone described above)[25] has led to the suggestion that an open-chain form makes a significant contribution to the sydnone structure in the solid state. Open-chain formulations are probably also of significance in 4,5-diphenylisosydnone[4] and in 3-phenyl-1,2,3,4-oxatriazolium-5-olate.[29] It was thus of interest to examine the *X*-ray molecular structure of one compound in the 1,2,4-triazolo[4,3-*a*]pyrimidinium betaine series with a view to assessing the importance of open-chain structures (**5A**).

The molecular structure of the betaine (**5b**), which is depicted in the Figure (ORTEP)[30a] together with the crystallographic numbering system adopted in this study, consists of well separated, discrete 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olate units. No significantly short intermolecular contacts within 3.4 Å were observed. In addition to the observed connectivity, the central heterocyclic ring system is essentially planar; the mean deviation from the least-squares plane through atoms C(1)–C(5) and N(1)–N(4) is ±0.004 Å. The carbonyl oxygen atom O(1) is also co-planar with the central ring system (the estimated deviation from the plane defined above is 0.007 Å). The most important bond distances and angles for non-hydrogen atoms are given in Table 5.

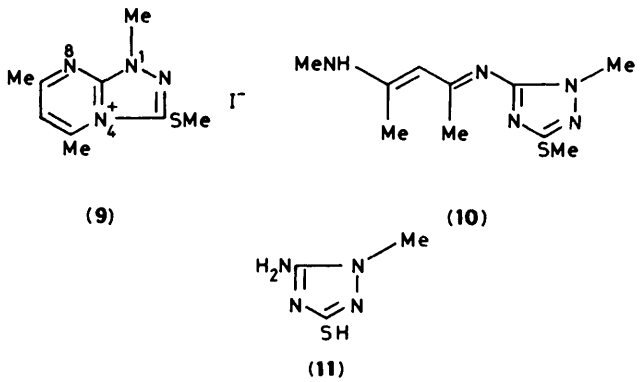
The betaine (**5b**) can be represented by either an open-chain structure (**8**) or by mesomeric ionic structures such as (**5b**), (**6**), and (**7**). The exocyclic C–O bond length* C(1)–O(1) [1.2269(23) Å] lies in the region associated with amides so that contributions such as (**6**) and (**8**) may be considered to be less important than (**5b**) and (**7**). In addition to this, the exocyclic N(1)–C(1)–O(1) bond angle distortion [129.63(18)°] is not so severe as that observed in the sydnone series (*e.g.* 135.8°)[25] and the C(1)–N(4) bond length [1.4540(22) Å] is normal for a C–N single bond [*cf.* 1.475 Å and 1.360 Å for the exocyclic N(1)–C bond and the C(3)–N(4) bond, respectively, in 1-(β-D-ribofuranosyl-1,2,4-triazole-3-carboxamide[30b]].

* In the ensuing discussion, the crystallographic numbering system (Figure) is used in describing bond distances in the betaine (**5b**).



An unexpected feature of the structure of the betaine (**5b**) is the importance of canonical form (**7**) to the overall representation: thus relatively short C–N bond lengths are observed for C(2)–N(2) [1.3137(21) Å] and C(3)–N(3) [1.3237(21) Å], and relatively long C–N bond lengths are noted for C(5)–N(4) [1.3557(26) Å], C(2)–N(3) [1.3450(21) Å], and C(2)–N(4) [1.3641(20) Å].

Reactions.—Compounds in the 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-thiolate (**5g**—**l**), but not those in the 3-olate series (**5a**—**f**), could be methylated by treatment with iodomethane in methanol at room temperature [see *e.g.* (**5g**) ⟶ (**9**)]. Similar results have been reported for mesoionic compounds containing exocyclic oxygen and sulphur atoms.[17] Treatment of the salt (**9**) with methylamine in methanol did not provide the expected 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-amide but gave a product with spectral and analytical data consistent with the triazole derivative (**10**). Formation of the latter can be explained by nucleophilic attack at C-5 of the salt (**9**) with ensuing fission of the C-5–N-4 bond, and has precedent in the base-promoted cleavage of heteroaromatic betaines in the xanthine series.[31] Cleavage of the pyrimidinium ring of the 3-thiolate (**5g**) is not induced by methylamine, but treatment with hydrazine hydrate under reflux causes extensive decomposition with formation of the triazole derivative (**11**).



The betaines (**5a**) and (**5g**) proved to be reactive towards the 1,3-dipolarophile dimethyl acetylenedicarboxylate (xylene, reflux) but complex mixtures were obtained from which no pure products could be isolated. This result is in contrast to our recent observations on such reactions of isomeric 1,2,4-triazolo[1,5-*a*]pyrimidinium-2-olates from which good yields of cycloadducts are formed.[32]

Experimental

M.p.s were determined on a Büchi 510 m.p. apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^{1}H N.m.r. spectra were obtained on Bruker WP-60 (60 MHz) or Bruker AM-250 (250 MHz) spectrometers with tetramethylsilane as internal standard. ^{13}C N.m.r. spectra were run on a Bruker AM-250 (250 MHz) spectrometer. Mass spectra were obtained using a VG-Micromass-16F spectrometer using a direct insertion probe. Merck Kieselgel 60 was used for column chromatography unless otherwise stated; for analytical t.l.c., pre-coated Merck Kieselgel 60 F 254 plates were used.

General Method for Preparation of Hydrazones (**2b**—**e**).—To a stirred slurry of sodium hydride (20 mmol) and THF (25 cm^3) at 30 °C was added a solution of benzaldehyde (4,6-dimethylpyrimidin-2-yl)hydrazone (**2a**) (20 mmol) in THF (60 cm^3) dropwise during 15 min. After being kept at 30 °C for a further 10 min, the mixture was treated with alkyl halide (20 mmol) and then heated under reflux for 2—10 h. The mixture was cooled to room temperature and diluted with water (100 cm^3). The resulting mixture was extracted with ethyl acetate (2 × 50 cm^3) and the combined extracts were dried (Na_2SO_4), and evaporated under reduced pressure. The residue was chromatographed on silica gel (Merck 7734) with ethyl acetate–hexane (15:85) as eluant and the product was recrystallised from the appropriate solvent. The following compounds were obtained [m.p. (°C), yield (%), and solvent for recrystallisation quoted]: (**2b**), 135.5—137, 83, EtOH; (**2c**), 111—112, 62, EtOAc; (**2d**), 91—93, 64, EtOAc; (**2e**), 67—68, 63, EtOAc. Analytical and spectral data are collected in the Supplementary Publication, Tables 1 and 2 respectively.*

General Method for the Preparation of Hydrazines (**2g**—**j**).—A solution of a hydrazone (**2b**—**e**) (10 mmol) in 2M-aqueous hydrochloric acid (60 cm^3) was heated under reflux for 4 h (benzaldehyde was removed from the reaction mixture by co-distillation with water). The solution was cooled to room temperature, then basified with 2M-aqueous sodium hydroxide, and the mixture was extracted with diethyl ether (2 × 50 cm^3). The combined extracts were dried (Na_2SO_4) and evaporated. The crude product was purified by distillation under reduced pressure in a Kugelrohr apparatus. The following compounds were obtained [oven temp. (°C)/pressure (mmHg) and yield (%) quoted]: (**2g**), 120/0.25, 77; (**2h**), 95/0.2, 84; (**2i**), 120/0.2, 90; (**2j**), 180/0.05, 90. Analytical and spectral data are collected in SUP 56702, Tables 3 and 4 respectively.

General Method for the Preparation of 1,2,4-*Triazolo*[4,3-a]*pyrimidinium Chlorides* (**3a**—**e**).—A solution of a hydrazine (**2f**—**j**) (4.4 mmol) in toluene (16 cm^3) was added to a vigorously stirred solution of phosgene (4.8 mmol) in toluene (13 cm^3) cooled to 5 °C. After the mixture had been stirred at room temperature for 2 h the product was filtered off, washed with hexane, and dried *in vacuo*. The hydrochlorides (**3a**), 95%; (**3b**), 88%; (**3c**), 90%; (**3d**), 100%; (**3e**), 92%) were thus obtained as pale yellow salts. These products could be used to prepare heteroaromatic betaines (**5b**—**e**) without further purification but one *compound*, (**3a**), (73%) was obtained analytically pure

* Supplementary data in Supplementary Publication SUP 56702 (11 pp.). For details of Supplementary Publications, see Notice to Authors No. 4, *J. Chem. Soc., Perkin Trans. 1*, 1988, issue 1, p. xvii.

(Found: C, 44.7; H, 5.1; N, 26.0. $C_8H_{11}ClN_4O$ requires C, 44.7; H, 5.1; N, 26.1%); δ_H (CD_3OD; 60 MHz) 2.67 (s, 3 H, 7-Me), 2.90 (d, *J* 1 Hz, 3 H, 5-Me), 3.93 (s, 3 H, NMe), and 7.05 (q, *J* 1 Hz, 1 H, 6-H); $\nu_{max.}$ (Nujol) 1 685 cm^{-1} (C=O); $\nu_{max.}$ (hexachlorobutadiene) 3 150 cm^{-1} (N–H).

General Method for the Preparation of 1,2,4-*Triazolo*[4,3-a]*pyrimidinium-3-olates* (**5a—e**).—Gaseous ammonia was bubbled into a slurry of a 1,2,4-triazolo[4,3-*a*]pyrimidinium chloride (**3**) (2.8 mmol) in chloroform (40 cm^3) during 5 min. The initial pale yellow mixture turned bright orange during the addition. The mixture was filtered, the filtrate was evaporated, and the crude product was purified by crystallisation. One such compound was 1,5,7-*trimethyl*-1H-1,2,4-*triazolo*[4,3-a]-*pyrimidinium-3-olate* (**5a**) (80%), m.p. 220 °C (decomp.) (from EtOH) (Found: C, 53.95; H, 5.7; N, 31.45. $C_8H_{10}N_4O$ requires C, 53.93; H, 5.61; N, 31.46%); $\nu_{max.}$($CHCl_3$) 1 680 (C=O) and 1 630 cm^{-1} (C=N); δ_H (CD_3OD; 250 MHz) 2.55 (s, 3 H, 7-Me), 2.90 (d, *J* 1.0 Hz, 3 H, 5-Me), 3.77 (s, 3 H, NMe), and 6.73 (q, *J* 1.0 Hz, 1 H, 6-H); δ_C (CD_3OD; 250 MHz) 15.72, 23.41, 32.16, 112.66, 144.10, 148.66, 150.01, and 173.73; *m/z* 178 (100%) ($M^{\cdot+}$), 136 (41, $M^{\cdot+}$ – NCO), 108 (17), and 107 (68).

The following compounds were also obtained [m.p. (°C), yield (%), and solvent for crystallisation quoted]: (**5b**), 176—178, 77, EtOAc/EtOH (2:1); (**5c**), 156—157, 68, EtOAc; (**5d**), 155—156, 66, EtOAc; (**5e**), 106—107, 74, EtOH. Analytical and spectroscopic data for compounds (**5b—e**) are collected in SUP 56702, Tables 5, 6, and 7.

Preparation 1-(3-*Hydroxypropyl*)-5,7-*dimethyl*-1H-1,2,4-*triazolo*[4,3-a]*pyrimidinium-3-olate* (**5f**).—A solution of boron trichloride (2 mmol) in dichloromethane (2 cm^3) was added during 10 min to a stirred solution of the benzyl ether (**5e**) (0.3 g, 0.96 mmol) in dichloromethane (20 cm^3) cooled to −10 °C. The mixture was warmed to room temperature and stirred for 1 h. Water (3 cm^3) was added, the mixture was evaporated under reduced pressure, and the residue was dissolved in methanol. Ammonia gas was bubbled through this solution for a period of 5 min. The resulting yellow solution was evaporated under reduced pressure and the residue was chromatographed [silica gel; chloroform–methanol (95:5) eluant] to give the yellow *title compound*, m.p. 144—145 °C (from EtOAc) (54%) (Found: C, 53.7; H, 6.2; N, 24.9. $C_{10}H_{14}N_4O_2$ requires C, 54.0; H, 6.2; N, 25.2%); $\nu_{max.}$($CHCl_2$) 3 520—3 120 (OH), 1 688 (C=O), and 1 630 cm^{-1} (C=N); δ_H [250 MHz; $(CD_3)_2C{=}O$] 2.07 (tt, *J* 6.3 and 6.9 Hz, 2 H, $CH_2CH_2CH_2$), 2.55 (s, 3 H, 7-Me), 2.91 (d, *J* 1 Hz, 3 H, 5-Me), 3.31 (t, *J* 6.3 Hz, 2 H, NCH_2), 3.62 (t, *J* 6.9 Hz, 2 H, OCH_2), and 6.73 (q, *J* 1 Hz, 1 H, 6-H); *m/z* 222 (41%) ($M^{\cdot+}$), 204 (18, $M^{\cdot+}$ – H_2O), 177 (39, $M^{\cdot+}$ – C_2H_4OH), 135 (13), and 108 (100).

Preparation of 1-(4,6-*Dimethylpyrimidin*-2-*yl*)-1-*methyl*-4-*phenylthiosemicarbazide* (**2k**).—Phenyl isothiocyanate (8.9 g, 66 mmol) was added to a solution of 1-(4,6-dimethylpyrimidin-2-yl)-1-methylhydrazine (**2f**) (10.0 g, 66 mmol) in ether (100 cm^3) at room temperature. The mixture was stirred for 3 h and the product was collected by filtration. Recrystallisation from ethanol gave the *title compound* (15.5 g, 82%), m.p. 143—144 °C (Found: C, 55.5; H, 5.9; N, 4.8. $C_{14}H_{17}N_5S$ requires C, 55.55; H, 5.9; N, 4.9%).

1,5,7-*Trimethyl*-1H-1,2,4-*triazolo*[4,3-a]*pyrimidinium-3-thiolate* (**5g**).—*Method A*. The thiosemicarbazide (**2k**) (1.0 g, 3.5 mmol) was heated at 220 °C for 40 min. The product was purified chromatographically (silica gel; $CHCl_3$ eluant) to give the orange *title compound*, m.p. 232—235 °C (from EtOH) (45%) (Found: C, 49.5; H, 5.2; N, 28.9. $C_8H_{10}N_4S$ requires C, 49.5; H, 5.2; N, 28.9%); $\nu_{max.}$($CHCl_3$) 1 632 cm^{-1} (C=N); δ_H [250 MHz; CD_3OD–$CDCl_3$ (5:2)] 2.62 (s, 3 H, 7-Me), 3.35 (d, *J* 1 Hz, 3 H, 5-Me), 3.90 (s, 3 H, NMe), and 6.87 (q, *J* 1 Hz, 1 H, 6-H); δ_C [250 MHz; CD_3OD–$CDCl_3$ (5:2)] 20.28, 24.92, 34.25, 114.79, 147.68, 153.15, 160.57, and 172.94; *m/z* 194 (46%, $M^{\cdot+}$), 162 (9), 137 (12), and 136 (44).

Method B. A solution of 4,6-dimethyl-2-(1-methylhydrazino)pyrimidine (**2f**) (1.0 g, 6.6 mmol) in chloroform (25 cm^3) was added dropwise during 15 min to a stirred solution of thiophosgene (0.6 cm^3) in chloroform (25 cm^3). The resulting yellow precipitate rapidly redissolved and the solution was stirred at room temperature overnight, and was then evaporated, and the residue was recrystallised from methanol to give the title compound (0.67 g, 47%), m.p. 232—235 °C. This compound was spectroscopically (i.r., ^1H n.m.r.) identical with the compound prepared by method A.

Method C. A mixture of 4,6-dimethyl-2-(1-methylhydrazino)pyrimidine (**2f**) (0.75 g, 5 mmol) and carbon disulphide (3.5 cm^3) in acetonitrile (10 cm^3) was stirred at room temperature for 2 days. Volatile materials were evaporated off under reduced pressure and the residue was recrystallised from ethanol to give the title compound (0.8 g, 83%), m.p. 232—235 °C. Method C was used to synthesize the related orange compounds (**5h—k**) [m.p. (°C), yield (%), and solvent for recrystallisation quoted]. (**5h**), 178—180, 81, EtOH; (**5i**), 178 (decomp.), 81, EtOAc; (**5j**), 166 (decomp.), 87, EtOH; (**5k**), 130—132, 79, EtOH. Analytical and spectral data for compounds (**5h—k**) are given in SUP 56702, Tables 8, 9, and 10.

Preparation of 1-(3-*Hydroxypropyl*)-5,7-*dimethyl*-1-H-1,2,4-*triazolo*[4,3-a]*pyrimidinium-3-thiolate* (**5l**).—The benzyl ether (**5k**) (0.3 g, 0.91 mmol) was deprotected using the procedure described for synthesis of the 3-olate analogue (**5f**). The pure *title compound* was obtained as orange needles (0.17 g, 76%), m.p. 179—180 °C (Found: C, 50.45; H, 5.95; N, 23.5. $C_{10}H_{14}N_4OS$ requires C, 50.4; H, 5.9; N, 23.5%); $\nu_{max.}$($CDCl_3$) 3 500—3 210 (OH) and 1 630 cm^{-1} (C=N); δ_H (250 MHz; CD_3OD) 2.11 (tt, *J* 6.1 and 7 Hz, 2 H, $CH_2CH_2CH_2$), 2.60 (s, 3 H, 7-Me), 3.37 (d, *J* 1 Hz, 3 H, 5-Me), 3.63 (t, *J* 6.1 Hz, 2 H, NCH_2), 4.39 (t, *J* 7.0 Hz, 2 H, OCH_2), and 6.90 (q, *J* 1 Hz, 1 H, 6-H); *m/z* 238 (99%, $M^{\cdot+}$), 220 (4, $M^{\cdot+}$ – H_2O), 178 (69, $M^{\cdot+}$ – C_3H_7OH), 180 (42, $M^{\cdot+}$ – NCS), 136 (49), 108 (100), and 107 (35).

1,5,7-*Trimethyl*-3-*methylthio*-1H-1,2,4-*triazolo*[4,3-a]*pyrimidinium Iodide* (**9**).—A solution of 1,5,7-trimethyl-1*H*-1,2,4-triazolo[4,3-*a*]pyrimidinium-3-thiolate (**5g**) (1.0 g, 5.1 mmol) and iodomethane (0.73 g, 5.1 mmol) in THF (60 cm^3) was stirred at room temperature for 2 h. After filtration the product was recrystallised from ethanol–diethyl ether to give the *title compound* (1.39 g, 80%), m.p. 250—252 °C (Found: C, 32.0; H, 3.9; N, 16.6. $C_9H_{13}IN_4S$ requires C, 32.15; H, 3.9; N, 16.7%); δ_H (60 MHz; CD_3OD) 2.76 (s, 3 H, 7-Me), 2.88 (s, 3 H, SMe), 3.06 (d, 3 H, 5-Me), 4.18 (s, 3 H, NMe), and 7.39 (m, 1 H, 6-H).

Reaction of 1,5,7-*Trimethyl*-3-*methylthio*-1H-1,2,4-*triazolo*[4,3-a]*pyrimidinium Iodide* (**9**) *with Methylamine*.—To a stirred solution of methylamine hydrochloride (0.27 g, 4 mmol) in dry methanol (10 cm^3) was added 5M-aqueous sodium hydroxide (0.8 cm^3, 4 mmol) followed by a solution of the salt (**9**) (0.67 g, 2 mmol) in methanol (10 cm^3). The resulting orange solution was stirred at room temperature for 1 h, and evaporated to dryness under reduced pressure, and the residue was partitioned between chloroform (30 cm^3) and water (10 cm^3). The organic phase was washed with water (10 cm^3), dried (Na_2SO_4), and evaporated to give a brown solid (0.4 g, 83%), recrystallisation of which from ethyl acetate–hexane gave the *triazole derivative* (**10**) as red-brown needles (0.35 g, 73%), m.p. 104.5—105.5 °C (Found: C, 50.2; H, 7.05; N, 29.2. $C_{10}H_{17}N_5S$ requires C, 50.2; H, 7.15; N, 29.25%); $\nu_{max.}$($CHCl_3$) 2 995, 1 620,

1 565, 1 457, 1 320, 1 292, 1 263, 1 083, and 1 020 cm^{-1}; δ_H (250 MHz; $CDCl_3$) 2.0 (s, 3 H, CMe), 2.2 (s, 3 H, CMe), 2.55 (s, 3 H, SMe), 2.99 (brs, 3 H, NMe), 3.63 (s, 3 H, NMe), and 4.78 (s, 1 H, olefinic H); δ_C [250 MHz; $(CD_3)_2CO$] 13.99, 19.31, 23.92, 29.84, 34.02, 97.01, 158.98, 159.25, 163.04, and 171.76; *m/z* 239 (59%, $M^{\cdot+}$), 224 (18), 209 (100), and 192 (32).

Reaction of 1,5,7-*Trimethyl*-1H-1,2,4-*triazolo*[4,3-a]*pyrimidinium*-3-*thiolate* (**5g**) *with Hydrazine Hydrate.*—The thiolate (**5g**) (0.20 g, 1 mmol) and hydrazine hydrate (5 cm^3) were heated together under reflux for 2 h. The solution was evaporated to dryness and the residue was triturated with diethyl ether to give 5-*amino*-1-*methyl*-1H-1,2,4-*triazole*-3-*thiol* (**11**) (0.13 g, 100%), m.p. 280 °C (decomp.) (Found: C, 27.7; H, 4.7; N, 42.8. $C_3H_6N_4S$ requires C, 27.7; H, 4.6; N, 43.1%); $\nu_{max.}$ (Nujol) 3 218 and 3 115 (NH_2) and 1 665 cm^{-1} (C=N); δ_H (CD_3OD–DCl) 3.73 (s, 3 H, Me); *m/z* 130 (100%, $M^{\cdot+}$).

Preparation of 5,7-*Dimethyl*-1,2,4-*triazolo*[4,3-a]*pyrimidin*-3(2H)-*one* (**4**).—A solution of 2-hydrazino-4,6-dimethylpyrimidine (**2**; R = $NHNH_2$) (0.5 g, 3.6 mmol) and pyridine (0.32 cm^3, 4 mmol) in THF (100 cm^3) was added to a solution of phosgene (4 mmol) in THF (40 cm^3) at room temperature during 20 min. The resulting orange mixture was stirred for 1 h, then filtered, and the residual solid was recrystallised from ethanol to give the *title compound* as yellow needles (0.15 g, 25%), m.p. 268 °C (decomp.) (Found: C, 51.05; H, 5.0; N, 34.0. $C_7H_8N_4O$ requires C, 51.2; H, 4.9; N, 34.15%); $\nu_{max.}$($CHCl_3$) 1 733 (C=O) and 1 643 cm^{-1} (C=N); δ_H [250 MHz; CD_3OD] 2.39 (s, 3 H, 7-Me), 2.75 (d, *J* 1 Hz, 3 H, 5-Me), and 6.35 (q, *J* 1 Hz, 1 H, 6-H); δ_C [250 MHz; $(CD_3)_2SO$] 16.20, 24.61, 108.00, 146.66, 147.14, 149.57, and 167.68; *m/z* 164 (93%, $M^{\cdot+}$) and 108 (100).

X-*Ray Crystal Structure of* 1-*Benzyl*-5,7-*dimethyl*-1H-1,2,4-*triazolo*[4,3-a]*pyrimidinium*-3-*olate* (**5b**).—*Crystal data.* $C_{14}H_{14}N_4O$, *M* = 240.3. Orthorhombic, *a* = 6.980 0(3), *b* = 15.352(1), *c* = 23.800 9(8) Å, space group *Pcab* (alt. *Pbca* No. 61), *Z* = 8, D_c = 1.251 g cm^{-3}, μ(Cu–K_α) = 6.20 cm^{-1}, *F*(000) = 1 016. The intensity data were collected on a CAD-4 diffractometer using Cu–K_α radiation in the range $1.5 < \theta < 65°$ with $\omega - 2\theta$ scanning, and corrected for Lorentz and polarisation effects but not for absorption. Of the 2 165 unique data measured, 1 574 reflections had $I > 2\sigma(I)$. The structure was solved by direct methods (SHELX 84)[33] and refined (SHELX 76)[34] by full-matrix least-squares methods (all non-hydrogen atoms anisotropic). The hydrogen atoms were readily located on difference-Fourier maps and included at idealised positions with isotropic group temperature factors except for the hydrogen atoms of the methyl groups at C(6) and C(7) which were found to be disordered. The disorder, which corresponded to the presence of two alternative, staggered conformations for each group, was modelled by the refinement of two relative site occupancy factors [at C(6) 50:50 and C(7) 76:24]. A weighting scheme $w = [\sigma^2(F) + 0.000\,18(F)^2]^{-1}$ was found to give satisfactory analyses of variance in ranges of |*F*| and sin θ. At convergence, the structural discrepancy factors *R* and R_w were 0.036 and 0.046 respectively with mean e.s.d.s of 0.002 Å for the bond lengths and 0.15° for the bond angles. The final difference-Fourier map contained no features greater than ±0.15 e $Å^{-3}$. Positional parameters for non-hydrogen atoms are listed in Table 6.*

* Tables of anisotropic temperature factors and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (see section 5.6.3 of Instructions for Authors, in the January issue).

Table 6. Fractional co-ordinates of atoms with standard deviations in parentheses

	x	*y*	*z*
N(1)	0.202 07(22)	−0.051 06(9)	0.469 77(7)
N(2)	0.153 52(20)	0.000 22(9)	0.423 57(6)
N(3)	0.152 09(19)	0.149 53(9)	0.396 84(6)
N(4)	0.252 46(19)	0.091 02(8)	0.486 21(5)
O(1)	0.322 01(21)	−0.011 96(9)	0.557 10(6)
C(1)	0.264 5(3)	0.003 59(12)	0.509 43(8)
C(2)	0.182 71(23)	0.083 51(10)	0.432 89(7)
C(3)	0.193 13(22)	0.227 64(10)	0.417 08(7)
C(4)	0.263 73(23)	0.240 40(11)	0.472 19(7)
C(5)	0.295 99(22)	0.172 38(11)	0.507 26(7)
C(6)	0.1659(3)	0.303 40(11)	0.378 41(8)
C(7)	0.3773(3)	0.180 17(13)	0.564 99(8)
C(8)	0.0882(3)	−0.038 88(13)	0.371 87(8)
C(9)	0.2488(3)	−0.069 78(11)	0.334 38(7)
C(10)	0.4114(3)	−0.020 01(14)	0.326 30(8)
C(11)	0.5523(3)	−0.045 79(16)	0.288 99(9)
C(12)	0.5310(5)	−0.121 75(18)	0.259 46(10)
C(13)	0.3741(5)	−0.172 80(17)	0.268 06(10)
C(14)	0.2328(4)	−0.147 48(13)	0.305 61(9)

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