Synthesis and Reactions of [1,2,4]Triazolo[1,5-*a*]pyrimidinium Betaines

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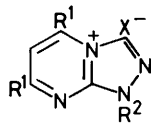
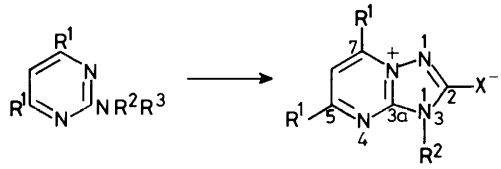
A number of 3-substituted [1,2,4]triazolo[1,5-*a*]pyrimidinium betaines have been synthesized and the reactions of these novel compounds has been investigated. Treatment of 2-alkylaminopyrimidines with phosgene gave 2-(*N*-alkyl-*N*-chlorocarbonylamino)pyrimidines (**2f—i**) which reacted with azidotrimethylsilane to yield 3-substituted [1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olates (**3a—d**). Analogous [1,2,4]triazolo[1,5-*a*]pyrimidinium-2-thiolates (**3f—i**) were obtained from the 2-olates by treatment with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulphide (Lawesson's reagent). The 3-hydroxypropyl derivatives (**3e**) and (**3j**) were prepared by deprotection of the benzyl ethers (**3d**) and (**3i**) using boron trichloride in dichloromethane at −10 °C. The 2-olates (**3a**) and (**3b**) reacted with dimethyl acetylenedicarboxylate to give the pyridine derivatives (**7a**) and (**7b**) and the 2-olate (**3b**) reacted regioselectively with methyl propiolate to provide the analogue (**7c**). Reaction of the 2-olates (**3a**) and (**3b**) with diphenylcyclopropenone gave 1,3-oxazin-6-ones (**12**). Evidence for the structure of one compound (**12b**) was adduced, in part, by transformation with ammonia into the pyrimidone (**13**) and with sodium methoxide into two separable isomers of the urea derivative (**14**).

Mesoionic compounds[1,2] and heteroaromatic betaines[3] are valuable in heterocyclic synthesis as 1,3-dipoles in cycloadditions. We recently reported the preparation of 1*H*-[1,2,4]-triazolo[4,3-*a*]pyrimidinium betaines (**1**)[4] which reacted with dipolarophiles to give, unfortunately, complex mixtures. Following our preliminary communication[5] we now provide full details of the synthesis and reactions of [1,2,4]triazolo[1,5-*a*]pyrimidinium betaines (**3**)



(1)

R^1 = Me
R^2 = Alkyl
X = O, S



(2) (3)

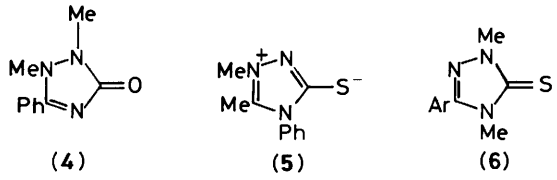
	R^1	R^2	R^3
a	H	Me	H
b	Me	Me	H
c	Me	Pr	H
d	Me	$(CH_2)_3OH$	H
e	Me	$(CH_2)_3OCH_2Ph$	H
f	H	Me	COCl
g	Me	Me	COCl
h	Me	Pr	COCl
i	Me	$(CH_2)_3OCH_2Ph$	COCl
j	Me	Me	CON_3

	R^1	R^2	X
a	H	Me	O
b	Me	Me	O
c	Me	Pr	O
d	Me	$(CH_2)_3OCH_2Ph$	O
e	Me	$(CH_2)_3OH$	O
f	H	Me	S
g	Me	Me	S
h	Me	Pr	S
i	Me	$(CH_2)_3OCH_2Ph$	S
j	Me	$(CH_2)_3OH$	S

Synthesis.—The [1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olates (**3a—d**) were prepared by modification of the method of Palazzo and Baiocchi[6] for the synthesis of analogous pyridinium betaines. Thus 2-alkylaminopyrimidines (**2a—c**) were prepared[7] following literature procedures and the hydroxypropyl derivative (**2d**) was obtained from 2-chloro-4,6-dimethylpyrimidine by reaction with 3-aminopropan-1-ol in 85% yield. The benzyl ether (**2e**) was prepared by alkylation of the hydroxy compound (**2d**) in moderate yield (51%) due to competing *N*-alkylation. The 2-alkylaminopyrimidines were treated with phosgene and the crude products distilled *in vacuo* to give pure 2-(*N*-alkyl-*N*-chlorocarbonylamino)pyrimidines (**2f—i**) in 70—80% yield. Reaction of the carbamoyl chlorides (**2f—i**) with azidotrimethylsilane in boiling toluene gave, *via* the carbamoyl azides, the 3-alkyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olates (**3a—d**) in 58—66% yield. The carbamoyl chloride (**2g**) gave the triazolo[1,5-*a*]pyrimidinium-2-olate (**3b**) (62% yield) together with the isomeric [1,2,4]triazolo[4,3-*a*]pyrimidinium-3-olate (**1**; $R^1 = R^2 = Me$, X = O)[4] (15% by n.m.r.), which was probably formed through Curtius rearrangement of the intermediate azide (**2j**) prior to cyclization. Deprotection of the benzyl ether (**3d**) by treatment with boron trichloride gave the hydroxypropyl derivative (**3e**), an analogue of the antiviral purine 9-(2-hydroxyethoxymethyl)guanine.[8]

A common method for conversion of exocyclic CO into CS bonds in mesoionic compounds involves reaction with triethyloxonium tetrafluoroborate followed by treatment of the ethyl ether with sodium sulphide or sodium hydrogen sulphide.[9] However, we have shown that thionation of [1,2,4]triazolo-[1,5-*a*]pyrimidinium-2-olates may be carried out directly using Lawesson's reagent.[10] Thus, the 2-olates (**3a—d**) and Lawesson's reagent (1.1 mol equiv.) in boiling toluene gave the [1,2,4]triazolo[1,5-*a*]pyrimidinium-2-thiolates (**3f—i**) in 62—78% yield. Deprotection of the benzyl ether (**3i**) gave the hydroxypropyl derivative (**3j**) in 68% yield.

Spectroscopic Properties.—Spectral data support the heteroaromatic betaine structure (**3**) for the 2-olates and 2-thiolates. The i.r. spectra of the 2-olates (**3a—e**) exhibit a strong C=O stretching band in the region 1 670—1 690 cm^{-1} close to values observed in mesoionic 1,2,4-triazolium-3-olates (1 660 cm^{-1}),[11] [1,2,4]triazolopyridiniumolates (1 660—1 670 cm^{-1})[6,12] and [1,2,4]triazolo[4,3-*a*]pyrimidinium-3-olates (1 680—1 690



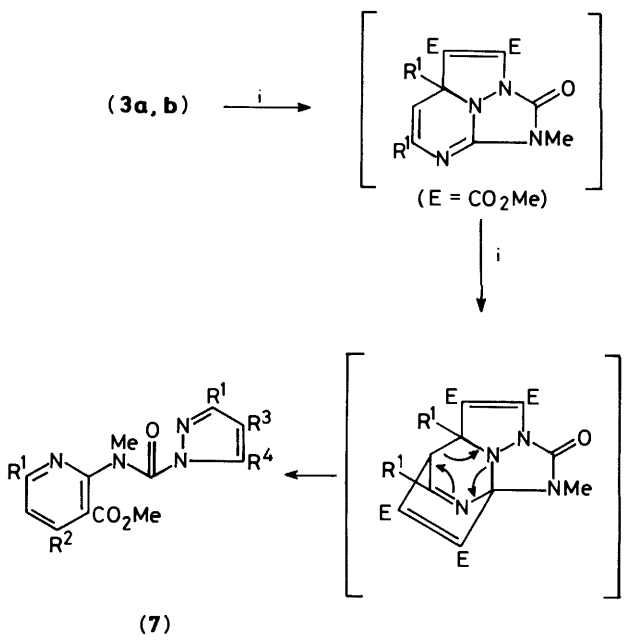
(4) (5) (6)

cm^{-1}).[4] The i.r. spectra of the 2-thiolates (**3f—j**) show a strong band in the region 1 315—1 340 cm^{-1} (C=S stretching) which is comparable to the absorption of mesoionic 1,2,4-triazolium-thiolates (1 320—1 330 cm^{-1}),[13] [1,2,4]triazolo[1,5-*a*]pyridinium-2-thiolates (1 380 cm^{-1}),[14] and [1,2,4]triazolo[4,3-*a*]-pyrimidinium-3-thiolates (1 345 cm^{-1}).[4]

Assignment of ^{13}C n.m.r. chemical shifts (Table 1) was based on analysis of spin-coupled spectra[15] and by comparison with model compounds.[16,17] In the ^{1}H n.m.r. spectra (Table 2) the 5-methyl and 7-methyl signals were unambiguously assigned using selective single frequency low power ^{1}H-{^{13}C} decoupling. The ^{13}C chemical shifts for the carbonyl carbon of the olates (**3a—d**) (*ca.* 160 p.p.m.) are close to those in model 1,2,4-triazol-3-ones [*e.g.* 162.2 p.p.m. in (**4**)[18]] suggesting substantial double bond character of the exocyclic bond. In contrast, the thiocarbonyl carbon in the thiolates (**3g—i**) appears at 170—174 p.p.m. which is to lower field than those in the 1,2,4-triazolium-3-thiolate (**5**) (168.32 p.p.m.)[19] and the 1,2,4-triazole-3-thione (**6**) (167.22 p.p.m.).[19] It may be concluded that the dipolar structure (**3**) makes a more important contribution to the resonance hybrid in the thiolate series (**3f—i**) than is the case in the olate series (**3a—e**). As expected, the resonances of the carbonyl carbon atoms and thiocarbonyl carbon atoms of the 1,2,4-triazolo[4,3-*a*]pyrimidinium-3-olates (**1**; X = O) and 3-thiolates (**1**; X = S) occur at higher field (10—14 p.p.m.)[4] than the analogous resonances of the 1,2,4-triazolo[1,5-*a*]pyrimidinium-2-olates (**2**; X = O) and 2-thiolates (**3**; X = S). This upfield shift may be attributed to the lesser deshielding effect of the adjacent bridgehead nitrogen atom in the [4,3-*a*] series. Similar observations have been reported for the ^{13}C n.m.r. spectra of covalent triazolopyrimidines and related heterocycles.[16,20]

A characteristic feature in the ^{1}H n.m.r. spectra of the 5,7-dimethyl derivatives of the [1,2,4]triazolo[1,5-*a*]pyrimidinium betaine ring system (**3**) is the selective coupling ($J \simeq 0.7$ Hz) of the 6-H and 7-Me substituents, a feature noted in the spectra of 'covalent' [1,2,4]triazolo[1,5-*a*]pyrimidines.[16,21] Such coupling may be attributed to the greater double bond character of the C(6)–C(7) bond compared to the C(5)–C(6) bond.

Reactions.—[1,2,4]Triazolo[1,5-*a*]pyrimidinium-2-olates (**3a, b**) reacted with dimethyl acetylenedicarboxylate (DMAD) in boiling xylene to give the pyridine derivatives (**7a, b**) in 62—65% yield, (Scheme 1). Analysis of the spectra of these compounds indicated that 1:2 adducts had been formed but did not permit unambiguous structure assignment, which was determined by *X*-ray crystallography.[5] Formation of the pyridines (**7a, b**) may be explained by a sequence of 1,3-dipolar cycloaddition, a hetero Diels–Alder reaction, and fragmentation of the pyrimidine and triazole rings of the adduct (see Scheme 1). The olate (**3b**) reacted regioselectively with methyl propiolate in boiling toluene to give a single crystalline product in 47% yield. The analytical and spectral data clearly showed that a 1:2 adduct of similar structure to pyridines (**7a, b**) had been formed. In principle, four possible isomers could be generated by the reactions in Scheme 1. However, the aromatic region of the ^{1}H n.m.r. spectrum exhibited an AB system (δ 7.3 and 8.11) thus excluding two isomers bearing a 4-methoxycarbonyl group (R^2) in the pyridine ring. A singlet (δ 8.46) was also present and comparison of the chemical shift with those of pyrazole model compounds [δ 6.76 (**8a**), δ 8.29 (**8b**)][22] suggests that isomer (**7c**)



(7)

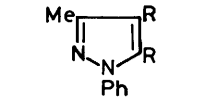
	R^1	R^2	R^3	R^4
a	H	CO_2Me	CO_2Me	CO_2Me
b	Me	CO_2Me	CO_2Me	CO_2Me
c	Me	H	CO_2Me	H
d	Me	H	H	CO_2Me

Scheme 1. *Reagents:* i, DMAD, reflux, xylene or toluene

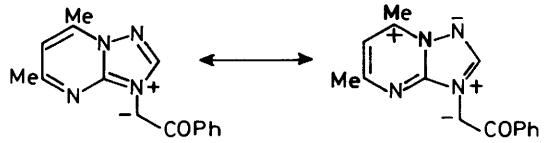
rather than (**7d**) is the correct structure. Thus these 1,3-dipolar cycloadditions proceed by [1,7] and not [1,3a] annulation as might be expected by comparison with the reactions of monocyclic [1,2,4]triazole mesoionic compounds.[23,24] This characteristic was also observed in the related double 1,3-dipolar cycloaddition of [1,2,4]triazolo[1,5-*a*]pyrimidinium ylides [*cf.* (**9**) ⟷ (**10**)] with dimethyl acetylenedicarboxylate and methyl propiolate recently reported[25] with selectivity through HOMO (dipole)-LUMO (dipolarophile) control.[26]

The unsubstituted [1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olates (**3a**) and the 2-thiolates (**3f—g**) reacted with DMAD to give complex mixtures from which no pure compounds could be isolated. Furthermore, no reaction occurred between the 2-olates (**3a, b**) or 2-thiolates (**3f, g**) and methyl acrylate, maleic anhydride, dimethyl maleate, diethyl azodicarboxylate, phenyl isocyanate, or phenyl isothiocyanate.

The [1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olates (**3a, b**) reacted with 1,3-diphenylcyclopropenone[27] (**11**) in boiling toluene or xylene to give the 1,3-oxazinones (**12**) in 34—36%



(**8**) R^1 R^2
a H CO_2Me
b CO_2Me H



(**9**) (**10**)

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

Carbon Compound	5	2	7	3a	6	NCH_2	5-CH_3	7-CH_3	Other
(**3a**)	151.82	160.25	134.87	145.80	112.5	26.31			
(**3b**)	161.79	159.97	146.05	145.39	112.40	26.36	24.26	16.99	
(**3c**)	161.60	159.85	145.90	145.29	112.19	42.05	21.50	17.03	11.46 (CH_3), 24.28 (CH_2)
(**3d**)	163.50	160.05	146.53	144.95	112.19	38.14	22.50	15.00	27.16, 67.65, 71.95 (CH_2)$_3$, 126.47, 126.58, 127.39, 137.84 (ArC)
(**3g**)	166.14	174.39	146.93	147.09	113.71	29.90	24.66	16.82	
(**3h**)	165.19	174.68	143.32	147.23	113.11	45.17	24.67	16.95	11.29 (CH_3), 21.11 (CH_2)
(**3i**)	164.84	170.11	145.94	146.25	112.84	41.34	24.34	16.58	27.41, 67.75, 72.40 (CH_2)$_3$, 127.06, 127.11, 127.96, 138.03 (ArC)

[a] Recorded at 62.9 MHz in $CDCl_3$ solution. Figures quoted (δ p.p.m.) are referred to tetramethylsilane.

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

Group Compound	5-CH_3	7-CH_3	6-H	NCH_2	Other
(**3a**)			7.32 dd (4, 6)	3.59 s	8.59 dd (2, 4) [5-H], 8.75 dd (2, 6) [7-H]
(**3b**)	2.60 s	2.69 d (0.7)	6.90 br, s	3.53 s	
(**3c**)	2.61 s	2.70 d (0.7)	6.90 br, d	3.99 t (6)	0.99 t (7) [CH_3], 1.89 tt (6, 7) [CH_2]
(**3d**)[b]	2.55 s	2.51 d (0.7)	6.98 br, d	4.12 t (6.6)	
(**3f**)[c]			7.51 dd (5, 8)	3.54 s	2.12 tt (6.5, 5.6) [CH_3], 3.59 t (5.6) [CH_2O], 4.32 s [CH_2], 7.1—7.3 m [ArH]
(**3g**)	2.68 s	2.78 d (0.7)	7.25 br, d	3.79 s	8.8 dd (2, 5) [5-H], 9.21 dd (2, 8) [7-H]
(**3h**)	2.63 s	2.76 d (0.7)	6.99 br, d	4.28 t (7.5)	
(**3i**)	2.61 s	2.69 d (0.7)	6.89 br, d	4.50 t (6.5)	0.98 t (7.5) [CH_3], 1.8—1.95 m [CH_2] 2.25 m [CH_2], 3.64 t (6) [CH_2O], 4.41 s [CH_2], 7.2—7.3 m [ArH]

[a] Recorded at 250 MHz in $CDCl_3$ solution unless otherwise stated. Figures quoted (δ p.p.m.) are referrred to tetramethylsilane. Coupling values *J* Hz are shown in parentheses. [b] In CD_3OD. [c] In $(CD_3)_2SO$.

yield (Scheme 2). The structural assignments were supported by spectral data and chemical transformations. For example, the carbonyl stretching frequency (1 730 cm^{-1}) in the i.r. spectra of compounds (**12a**, **b**) is similar to those reported for 1,3-oxazinones (1 735—1 760 cm^{-1}).[28] Reaction of compound (**12b**) with ammonia in methanol gave the pyrimidinone (**13**) in 84% yield. Compound (**13**) exhibited a strong carbonyl absorption at 1 662 cm^{-1} in the i.r. spectrum which is in good agreement to that observed (1 663 cm^{-1}) for the pyrimidinone (**15**).[28] Opening of the oxazinone ring of compound (**12b**) with sodium methoxide in methanol gave a mixture of two urea derivatives (**14**) (56% yield) which were separated. Spectroscopic properties of the compounds indicated that the products were *E*- and *Z*-(**14**).

No reaction was observed between [1,2,4]triazolo[1,5-*a*]pyrimidinium-2-thiolates (**3f**, **g**) and 1,3-diphenylcyclopropenone. However, the 2-thiolate (**3g**) but not the 2-olate (**3b**) reacted with iodomethane to give the salt (**16**).

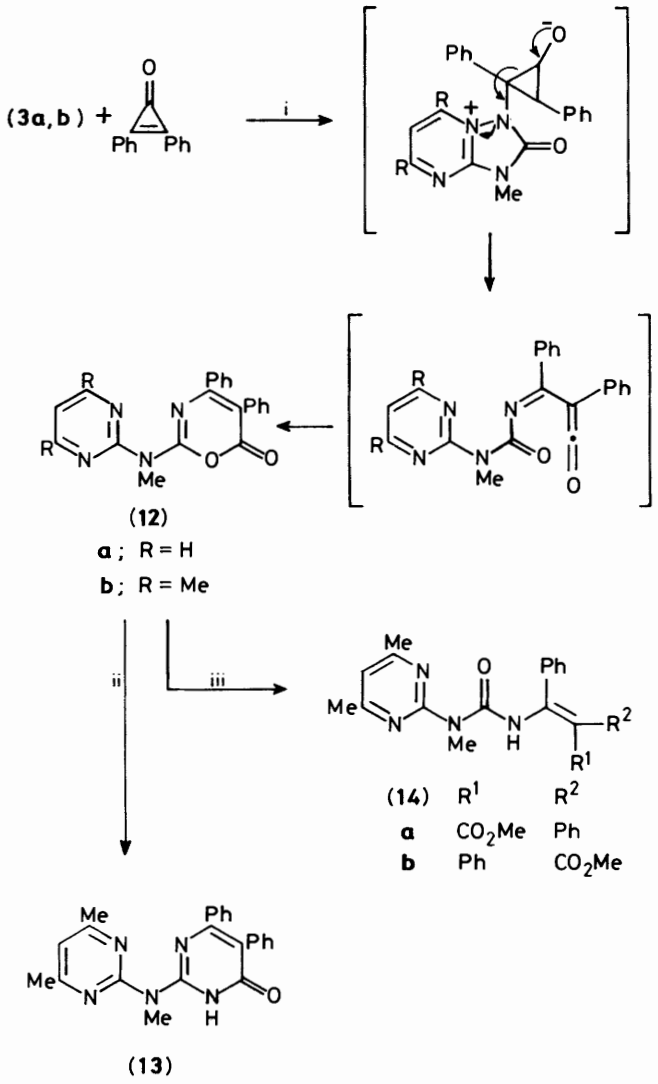
Experimental

M.p.s were determined on a Buchi 510 m.p. apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^1H 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.

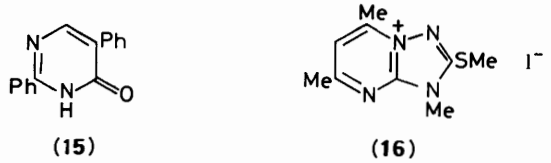
Reagents.—Ether refers to diethyl ether. 2-Methylaminopyrimidine (**2a**),[29] 4,6-dimethyl-2-methylaminopyrimidine (**2b**)[30] and 4,6-dimethyl-2-propyl aminopyrimidine (**2c**)[31] were prepared by literature procedures.

2-(3-*Hydroxypropylamino*)-4,6-*dimethylpyrimidine* (**2d**).—3-Aminopropan-1-ol (0.75 ml, 0.144 mol) and 2-chloro-4,6-dimethylpyrimidine[31] (5.0 g, 0.035 mol) in ethanol (75 ml) were heated under reflux for 18 h. The solution was then cooled, evaporated under reduced pressure, and the residue partitioned between chloroform (100 ml) and water (75 ml). The organic layer was separated, washed with water (2 × 75 ml), dried (Na_2SO_4), and evaporated under reduced pressure. The crude product was purified by Kugelrohr distillation (oven temp. 140 °C; pressure 0.25 Torr) to give the title compound (**2d**) as a colourless oil which slowly crystallized with time (5.4 g, 85%), m.p. 48—49 °C (Found: C, 59.5; H, 8.2; N, 23.0. $C_9H_{15}N_3O$ requires C, 59.65; H, 8.3; N, 23.2%); $\nu_{max.}$(liquid film) 3 600—3 100 (OH) and 1 545 cm^{-1}; $\delta_H(CD_3OD)$ 1.50—2.00 (m, 2 H, CH_2), 2.26 (s, 6 H, 4-CH_3 and 6-CH_3), 3.32—3.83 (m, 4 H, OCH_2 and NCH_2), 6.37 (s, 1 H); *m/z* (%) 181 (M^+, 35), 151 (13), 150 (60), 137 (68), 136 (100), 123 (32), 108 (29), 107 (23), and 67 (27).

2-(3-*Benzyloxypropylamino*)-4,6-*dimethylpyrimidine* (**2e**).—Sodium hydride (55% dispersion in oil; 0.97 g, 22 mmol) was added, in portions over 30 min, to a stirred solution of 2-(3-hydroxypropylamino)-4,6-dimethylpyrimidine (**2d**) (4.0 g, 22 mmol) in toluene (75 ml) at room temperature. The mixture was heated at 70 °C for 30 min, benzyl bromide (3.76 g, 22 mmol) was added, and the mixture heated under reflux for 1 h. T.l.c. analysis [SiO_2; EtOAc–hexane (1:1), u.v.] showed three products at R_F 0.3, 0.45, and 0.9. The mixture was cooled, water (25 ml) was added, and the phases were separated. The organic layer was dried (Na_2SO_4), evaporated under reduced pressure and the residue chromatographed on silica gel using ethyl



Scheme 2. An alternative mechanism to the one presented is possible in which initial nucleophilic attack at the 1,3-diphenylcyclopropenone is by the exocyclic oxygen of the 2-olates (**3a, b**). *Reagents:* i, xylene reflux; ii, NH_3, MeOH r.t.; iii, NaOMe, MeOH r.t.



acetate–hexane (15:85) as eluant. The following compounds were obtained.

2-[*N*-(3-Benzyloxypropyl)-*N*-benzylamino]-4,6-dimethylpyrimidine (0.8 g, 10%) (R_F 0.9) (Found: C, 76.5; H, 7.5; N, 11.75. $C_{23}H_{27}N_3O$ requires C, 76.4; H, 7.55; N, 11.6%); $\nu_{max.}$(thin film) 1 568, 1 505, and 698 cm^{-1}; $\delta_H(CDCl_3)$ 1.93 (tt, 2 H, *J* 7 Hz, CH_2), 2.24 (s, 6 H, 2 × CH_3), 3.49 (t, 2 H, *J* 6.5 Hz, OCH_2), 3.68 (t, 2 H, *J* 6.5 Hz, NCH_2), 4.49 (s, 2 H, CH_2Ph), 4.95 (s, 2 H, CH_2Ph), 6.40 (s, 1 H, 5-H), and 7.21—7.37 (m, 10 H, ArH).

2-[*N*-(3-Hydroxypropyl)-*N*-benzylamino]-4,6-dimethylpyrimidine (1.0 g, 18%) (R_F 0.3) (Found: C, 70.6; H, 7.75; N, 15.6. $C_{16}H_{21}N_3O$ requires C, 70.8; H, 7.8; N, 15.5%); $\nu_{max.}$(thin film) 3 600—3 100 (OH) and 1 575 cm^{-1}; $\delta_H(CD_3OD$, 60 MHz) 1.69 (m, 2 H, CH_2), 2.28 (s, 6 H, 4-CH_3 and 6-CH_3), 3.50 (t, 2 H, *J* 6 Hz, OCH_2), 3.60 (t, 2 H, *J* 6 Hz, NCH_2), 4.91 (s, 2 H, CH_2Ph), 6.41 (s, 1 H, 5-H), 7.28 (s, 5 H, ArH).

2-(3-Benzyloxypropylamino)-4,6-dimethylpyrimidine (**2e**) (3.0 g, 51%) (R_F 0.45); b.p. 200 °C at 0.5 Torr (Kugelrohr) (Found: C, 70.7; H, 7.85; N, 15.4. $C_{16}H_{21}N_3O$ requires C, 70.8; H, 7.8; N, 15.5%); $\nu_{max.}$(thin film) 3 280 (NH) and 1 575 cm^{-1}; $\delta_H(CD_3OD$, 60 MHz) 1.89 (m, 2 H, CH_2), 2.28 (s, 6 H, 4-CH_3 and 6-CH_3), 3.47 (t, 2 H, *J* 6 Hz, OCH_2), 3.57 (t, 2 H, *J* 6 Hz, NCH_2), 4.51 (s, 2 H, CH_2Ph), 6.38 (s, 1 H, 5-H), and 7.32 (s, 5 H, ArH); *m/z* (%) 272 (M^+, 25), 180 (67), 165 (23), 164 (13), 123 (23), 122 (17), 108 (11), 107 (14), 91 (38), and 67 (15).

General Procedure for the Preparation of 2-(N-*Alkyl*-N-*chlorocarbonylalkylamino*)*pyrimidines* (**2f—i**).—To a vigorously stirred solution of phosgene (0.1 mol) in toluene (500 ml) at 5 °C was added a solution of the 2-(*N*-alkylamino)pyrimidine (0.1 mol) and pyridine (0.1 mol) in toluene (500 ml), dropwise over 40 min. The mixture was allowed to warm to room temperature, and then heated at 40 °C for 30 min. The mixture was cooled, filtered, and the filtrate was evaporated under reduced pressure. The crude product was purified by distillation under reduced pressure in a Kugelrohr apparatus. The following compounds were prepared.

2-(N-*Chlorocarbonyl*-N-*methylamino*)*pyrimidine* (**2f**). Colourless liquid (12.0 g, 70%), b.p. 120 °C/0.4 Torr (Found: C, 42.15; H, 3.85; N, 24.3. $C_6H_6ClN_3O$ requires C, 42.0; H, 3.55; N, 24.5%); $\nu_{max.}$(thin film) 1 750 cm^{-1} (C=O); $\delta_H[(CD_3)_2CO]$ 3.53 (s, 3 H, NCH_3), 7.52 (t, 1 H, *J* 5 Hz, 5-H), and 8.43 (d, 2 H, *J* 5 Hz, 4-H and 6-H).

2-(N-*Chlorocarbonyl*-N-*methylamino*)-4,6-*dimethylpyrimidine* (**2g**). Colourless liquid (17.6 g, 88%), b.p. 100 °C/0.2 Torr (Found: C, 48.1; H, 5.15; N, 20.95. $C_8H_{10}ClN_3O$ requires C, 48.15; H, 5.0; N, 21.05%); $\nu_{max.}$(thin film) 1 750 cm^{-1} (C=O); $\delta_H[(CD_3)_2CO]$ 2.48 (d, 6 H, *J* 0.5 Hz, 4-CH_3 and 6-CH_3), 3.46 (s, 3 H, NCH_3), and 7.23 (s, 1 H, 5-H).

2-(N-*Chlorocarbonyl*-N-*propylamino*)-4,6-*dimethylpyrimidine* (**2h**). Colourless liquid (1.8 g, 79%), b.p. 135 °C/0.3 Torr (Found: C, 52.8; H, 6.35; N, 18.6. $C_{10}H_{14}ClN_3O$ requires C, 52.75; H, 6.2; N, 18.5%); $\nu_{max.}$(thin film) 1 740 cm^{-1} (C=O); $\delta_H(CDCl_3)$ 0.92 (t, 3 H, *J* 6 Hz, CH_3), 1.35 (m, 2 H, CH_2), 2.25 (s, 6 H, 4-CH_3 and 6-CH_3), 3.94 (t, 2 H, *J* 6 Hz, NCH_2), 6.99 (s, 1 H, 5-H); *m/z* (%) 227 (M^+, 22).

2-(N-*Benzyloxypropyl*-N-*chlorocarbonylamino*)-4,6-*dimethylpyrimidine* (**2i**). Brown oil (3.2 g, 95%), $\nu_{max.}$(thin film) 1 740 cm^{-1} (C=O); $\delta(CDCl_3)$ 1.95—2.10 (m, 2 H, CH_2), 2.48 (d, 6 H, *J* 0.5 Hz, 4-CH_3 and 6-CH_3), 3.55 (t, 2 H, *J* 6 Hz, OCH_2), 4.10 (t, 2 H, *J* 7 Hz, NCH_2), 4.39 (s, 2 H, CH_2Ph), 6.94 (s, 1 H, 5-H), 7.13—7.36 (m, 5 H, ArH); *m/z* (%) 334 (M + 1, 11), 273 (10), 272 (54), 241 (42), 180 (22), 136 (27), 92 (38), 91 (72), and 75 (100).

General Procedure for the Preparation of [1,2,4]*Triazolo*-[1,5-a]*pyrimidinium*-2-*olates* (**3a—d**).—Azodotrimethylsilane (55 mol) was added to a stirred solution of the 2-(*N*-alkyl-*N*-chlorocarbonylamino)pyrimidine (50 mmol) in dry toluene (300 ml) and the solution heated under reflux for 18 h. The mixture was cooled to room temperature and evaporated under reduced pressure. The residue was chromatographed on silica gel using chloroform–methanol (98:2) as eluant and the product recrystallized from the appropriate solvent. The following compounds were prepared and the n.m.r. data are collected in Tables 1 and 2.

3-*Methyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*olate* (**3a**). Pale yellow needles (4.4 g, 59%), m.p. 246 °C (MeOH) (Found: C, 47.9; H, 4.1; N, 37.2. $C_6H_6N_4O$ requires C, 48.0; H, 4.05; N, 37.3%); $\nu_{max.}(CHCl_3)$ 1 675 (C=O), 1 635, and 1 575 cm^{-1}; *m/z* (%) 150 (M^+, 100), 108 (26), 93 (11), 80 (19), 79 (10), 67 (74), 66 (21), 53 (24), 52 (11), and 41 (14).

3,5,7-*Trimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*olate*

(**3b**). Pale yellow needles (6.1 g, 62%), m.p. 244 °C (decomp.) (toluene) (Found: C, 53.7; H, 5.6; N, 31.4. $C_8H_{10}N_4O$ requires C, 53.9; H, 5.65; N, 31.45%); $\nu_{max.}$($CHCl_3$) 1 670 (C=O), 1 633, and 1 580 cm^{-1}; *m/z* (%) 178 (M^+, 100), 136 (43), 108 (23), and 107 (32).

5,7-*Dimethyl*-3-*propyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*olate* (**3c**). Colourless needles (1.3 g, 58%), m.p. 135—136 °C [EtOH—Et_2O (1:1)] (Found: C, 58.25; H, 6.85; N, 27.2. $C_{10}H_{14}N_4O$ requires C, 58.25; H, 6.8, N, 27.2%); $\nu_{max.}$($CHCl_3$) 1 687 (C=O), 1 630, and 1 570 cm^{-1}; *m/z* (%) 206 (M^+, 17), 200 (26), 199 (47), 178 (22), 165 (27), 164 (100), 136 (64), 108 (47), 67 (41), and 61 (48).

3-(3-*Benzyloxypropyl*)-5,7-*dimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*olate* (**3d**). Tan plates (0.9 g, 66%), m.p. 107—108 °C (EtOAc) (Found: C, 65.4; H, 6.45; N, 17.9. $C_{17}H_{20}N_4O_2$ requires C, 65.35; H, 6.45; N, 17.95%); $\nu_{max.}$($CHCl_3$) 1 680 (C=O), 1 630, and 1 570 cm^{-1}; *m/z* (%) 312 (M^+, 6), 221 (54), 178 (60), 165 (100), 164 (69), 163 (25), 150 (53), 136 (49), and 108 (41).

3-(3-*Hydroxypropyl*)-5,7-*dimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*olate* (**3e**).—Boron trichloride (3.6 mmol) in dichloromethane (3.6 ml) was added to a stirred solution of 3-(3-benzyloxypropyl)-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olate (**3d**) (0.55 g, 1.8 mmol) in dichloromethane at −20 °C. The solution was allowed to warm to room temperature over 1 h whereupon methanol (1 ml) was added. Ammonia gas was bubbled through the solution for 2 min and the precipitated ammonium chloride filtered off. The yellow filtrate was evaporated under reduced pressure and the residue triturated with ether to give the title compound (**3e**) as a yellow solid (300 mg, 77%). An analytical sample was prepared by recrystallization from ethyl acetate; m.p. 192—194 °C (tan prisms) (Found: C, 54.15; H, 6.35; N, 25.1. $C_{10}H_{14}N_4O_2$ requires C, 54.0; H, 6.35; N, 25.2%); $\nu_{max.}$($CHCl_3$) 3 600—3 100 (OH), 1 665 (C=O), 1 630, and 1 570 cm^{-1}; δ_H(CD_3OD) 2.02 (tt, 2 H, *J* 6.2 and 6.9 Hz, CH_2), 2.62 (s, 3 H, 5-CH_3), 2.67 (d, 3 H, *J* 0.7 Hz, 7-CH_3), 3.64 (t, 2 H, *J* 6.2 Hz, OCH_2), 4.10 (t, 2 H, *J* 6.9 Hz, NCH_2), 7.17 (br d, 1 H, 6-H); δ_C(CD_3OD) 14.71 (7-CH_3), 22.19 (5-CH_3), 29.90 (CH_2), 36.79 (OCH_2), 57.96 (NCH_2), 112.06 (C-6), 144.50 (C-3a), 146.57 (C-7), 159.76 (C-2), 163.02 (C-5); *m/z* (%) 222 (M^+, 17), 221 (24), 206 (19), 178 (100), 165 (74), 164 (69), 150 (25), 136 (90), 108 (49), 107 (17), and 91 (40).

General Method for the Preparation of [1,2,4]*Triazolo*[1,5-a]-*pyrimidinium*-2-*olates* (**3f—i**).—A mixture of the [1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olate (**3a—d**) (2.5 mmol) and 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulphide (Lawesson's reagent) (1.4 mmol) in dry toluene (50 ml) was heated under reflux for 5–10 h. The mixture was cooled and the product filtered off and purified by recrystallization. The following compounds, the n.m.r. data for which are collected in Tables 1 and 2, were prepared.

3-*Methyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*thiolate* (**3f**). Yellow needles (0.26 g, 62%), m.p. 278 °C (decomp.) (AcOH). (Found: C, 43.35; H, 3.65; N, 33.4. $C_6H_6N_4S$ requires C, 43.35; H, 3.65; N, 33.7%); $\nu_{max.}$(Nujol) 1 620, 1 540, 1 332 (C=S), 810, and 750 cm^{-1}; *m/z* (%) 166 (M^+, 100).

3,5,7-*Trimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*thiolate* (**3g**). Yellow needles (0.38 g, 78%), m.p. 258 °C (decomp.) (MeOH) (Found: C, 49.5; H, 5.2; N, 28.85. $C_8H_{10}N_4S$ requires C, 49.45; H, 5.2; N, 28.85%); $\nu_{max.}$($CHCl_3$) 1 630, 1 586, and 1 335 cm^{-1} (C=S); *m/z* (%) 194 (M^+, 73), 211 (15), 189 (34), 181 (23), 180 (100), and 166 (45).

5,7-*Dimethyl*-3-*propyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*thiolate* (**3h**). Colourless needles (0.36 g, 65%), m.p. 209—211 °C [dichloromethane—hexane (2:1)] (Found: C, 54.0; H, 6.35; N, 25.0. $C_{10}H_{14}N_4S$ requires C, 54.0; H, 6.35; N, 25.1%); $\nu_{max.}$($CHCl_3$) 1 625, 1 568, and 1 340 cm^{-1} (C=S); *m/z* (%) 222 (M^+, 86), 211 (15), 189 (34), 181 (23), 180 (100), and 166 (45).

3-(3-*Benzyloxypropyl*)-5,7-*dimethyl*-1,2,4-*triazolo*[1,5-a]-*pyrimidinium*-2-*thiolate* (**3i**). Tan needles (0.53 g, 68%), m.p. 134—136 °C (MeOH) (Found: C, 62.0; H, 6.15; N, 16.9. $C_{17}H_{20}N_4S$ requires C, 62.2; H, 6.15; N, 17.05%); $\nu_{max.}$($CHCl_3$) 1 625, 1 568, and 1 340 cm^{-1} (C=S); *m/z* (%) 328 (M^+, 57), 295 (36), 181 (82), 180 (49), 108 (36), 107 (34), 91 (95), 41 (55), and 28 (100).

3-(3-*Hydroxypropyl*)-5,7-*dimethyl*[1,2,4]*triazolo*[1,5-*a*]*pyrimidinium*-2-*thiolate* (**3j**).—Boron trichloride (0.86 mmol) in dichloromethane (1 ml) was added to a stirred solution of 3-(3-benzyloxypropyl)-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-thiolate (**3i**) (140 mg, 0.43 mmol) in dichloromethane (5 ml) at −20 °C. The mixture was allowed to warm to room temperature over 1 h whereupon methanol (1 ml) was added. The mixture was evaporated under reduced pressure and the residue chromatographed on silica gel using chloroform–methanol (95:5) as eluant. The product was recrystallized from dichloromethane–hexane (1:1) to give 3-hydroxypropyl-5,7-dimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-thiolate (**3j**) as white needles (68 mg, 68%), m.p. 212—214 °C (Found: C, 50.3; H, 5.9; N, 23.3.$C_{10}H_{14}N_4OS$ requires C, 50.4; H, 5.9; N, 23.5%); $\nu_{max.}$($CHCl_3$) 3 580—3 100 (OH), 1 628, 1 569, 1 335 (C=S), and 1 192 cm^{-1}; *m/z* (%) 238 (M^+, 61), 224 (11), 210 (22), 207 (23), 205 (100), 194 (54), 181 (24), 108 (79), 107 (39), and 83 (86).

Reaction of 3-*Methyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*olate* (**3a**) *with Dimethyl Acetylenedicarboxylate.*—Dimethyl acetylenedicarboxylate (3.3 g, 23.5 mmol) was added to a stirred mixture of 3-methyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olate (**3a**) (1.0 g, 6.7 mmol) in dry xylene (60 ml) and the mixture heated under reflux for 24 h. The mixture was cooled, evaporated under reduced pressure, and the residue chromatographed on silica gel using ethyl acetate–hexane (25:75) as eluant. The product was recrystallized from ethyl acetate–hexane to give *N*-(3,4-dimethoxycarbonyl-2-pyridyl)-*N*-methyl-4,5-dimethoxycarbonylpyrazole-1-carboxamide (**7a**) as colourless prisms (1.8 g, 62%), m.p. 152—153 °C (Found: C, 49.9; H, 4.2; N, 12.9. $C_{18}H_{18}N_4O_9$ requires C, 49.8; H, 4.2; N, 12.9%); $\nu_{max.}$(Nujol) 1 757, 1 740, 1 725, and 1 710 cm^{-1} (C=O); δ_H($CDCl_3$) 3.53 (s, 3 H, NCH_3), 3.80 (s, 3 H, CO_2CH_3), 3.88 (s, 3 H, CO_2CH_3), 3.92 (s, 3 H, CO_2CH_3), 4.03 (s, 3 H, CO_2CH_3), 7.57 (s, 1 H, ArH), 7.73 (d, 1 H, *J* 5 Hz, ArH), 8.69 (d, 1 H, *J* 5 Hz, ArH); *m/z* (%) 434 (M^+, 1), 376 (17), 375 (100), 251 (60), 207 (12), 153 (11), 106 (13), 79 (14), and 44 (19).

Reaction of 3,5,7-*Trimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium*-2-*olate* (**3b**) *with Dimethyl Acetylenedicarboxylate.*—Dimethyl acetylenedicarboxylate (0.48 g, 3.5 mmol) was added to a stirred mixture of 3,5,7-trimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olate (**3b**) (0.18 g, 1 mmol) in dry xylene (30 ml) and the mixture heated under reflux for 24 h. The mixture was cooled, evaporated under reduced pressure, and the residue chromatographed on silica gel using ethyl acetate–hexane (20:80) as eluant. The product was recrystallized from ethyl acetate–hexane to give *N*-(3,4-dimethoxycarbonyl-6-methyl-2-pyridyl)-*N*-methyl-4,5-dimethoxycarbonyl-3-methylpyrazole-1-carboxamide (**7b**) as colourless prisms (0.3 g, 65%), m.p. 145—146 °C (Found: C, 51.95; H, 4.8; N, 12.1.$C_{20}H_{22}N_4O_9$ requires C, 51.95; H, 4.8; N, 12.1%); $\nu_{max.}$($CHCl_3$) 1 725 cm^{-1} (C=O); δ_H($CDCl_3$) 2.06 (s, 3 H, CH_3), 2.64 (d, 3 H, *J* 0.3 Hz, CH_3), 3.50 (s, 3 H, NCH_3), 3.77 (s, 3 H, CO_2CH_3), 3.83 (s, 3 H, CO_2CH_3), 3.88 (s, 3 H, CO_2CH_3), 3.99 (s, 3 H, CO_2CH_3), 7.53 (d, 1 H, *J* 0.3 Hz, ArH); δ_C[$(CD_3)_2CO$] 13.41, 24.19, 29.62, 38.61, 51.79, 53.28, 53.31, 112.98, 121.55, 122.84, 139.94, 140.43, 148.64, 151.06, 153.05, 160.99, 161.21, 162.13, 165.06, 165.43; *m/z* (%) 462

(M^+, 2), 403 (31), 373 (14), 266 (14), 265 (100), 221 (13), 181 (15), 180 (11), 120 (19), and 93 (20).

Reaction of 3,5,7-*Trimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium-2-olate* (**3b**) *with Methyl Propiolate.*—Methyl propiolate (0.5 g, 6 mmol) was added to a stirred mixture of 3,5,7-trimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olate (**3b**) (0.3 g, 1.7 mmol) in dry xylene (15 ml) and the mixture heated under reflux for 48 h. The mixture was cooled and evaporated under reduced pressure and the residue chromatographed on silica gel using ethyl acetate–hexane (20:80) as eluant. The product was recrystallized from ethyl acetate–hexane (1:4) to give *N*-(3-methoxycarbonyl-6-methyl-2-pyridyl)-*N*-methyl-3-methyl-4-methoxycarbonylpyrazole-1-carboxamide (**7c**) as tan crystals (0.25 g, 47%), m.p. 95—97.5 °C (Found: C, 55.6; H, 5.3; N, 16.15. $C_{16}H_{18}N_4O_5$ requires C, 55.5; H, 5.25; N, 16.2%); $\nu_{max.}$($CHCl_3$) 1 720 (C=O) and 1 270 cm^{-1}; δ_H($CDCl_3$) 2.01 (s, 3 H, CH_3), 2.52 (s, 3 H, CH_3), 3.51 (s, 3 H, NCH_3), 3.72 (s, 3 H, CO_2CH_3), 3.76 (s, 3 H, CO_2CH_3), 7.31 (dq, 1 H, *J* 8 and 0.49 Hz, ArH), 8.11 (dq, 1 H, *J* 8.0 and 0.16 Hz, ArH), and 8.46 (q, 1 H, *J* 0.4 Hz, ArH); *m/z* (%) 346 (M^+, 2), 315 (3), 288 (17), 287 (100), 270 (13), 268 (8), 208 (34), 207 (58), 206 (26), 163 (18), 150 (18), and 92 (19).

Reaction of 3-*Methyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium-2-olate* (**3a**) *with Diphenylcyclopropenone.*—A mixture of 3-methyl-[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olate (**3a**) (200 mg, 1.33 mmol) and diphenylcyclopropenone (302 mg, 1.47 mmol) in toluene (20 ml) was heated under reflux for 72 h. The mixture was then cooled and evaporated under reduced pressure and the residue chromatographed on silica gel using dichloromethane–methanol (99:1) as eluant. The product was recrystallized from methanol to give 4,5-diphenyl-2-(*N*-pyrimidin-2-yl-*N*-methylamino)-1,3-oxazin-6-one (**12a**) as colourless needles (170 mg, 34%), m.p. 174.5—176 °C (Found: C, 70.75; H, 4.65; N, 15.6. $C_{21}H_{16}N_4O_2$ requires C, 70.8; H, 4.55; N, 15.7%); $\nu_{max.}$(Nujol) 1 730 cm^{-1} (C=O); δ_H(CD_2Cl_2) 3.77 (s, 3 H, NCH_3), 7.16 (t, 1 H, *J* 4 Hz, H-5), 7.17—7.42 (m, 10 H, ArH), and 8.72 (d, 2 H, *J* 4 Hz, 4-H and 6-H); δ_C(CD_2Cl_2) 36.71, 112.17, 118.05, 127.91, 128.08, 128.56, 129.98, 130.27, 131.33, 134.08, 138.05, 160.47, 160.97, and 162.3; *m/z* (%) (M^+, 54), 328 (30), 314 (56), 248 (37), 226 (12), 225 (77), 192 (100), 190 (22), 166 (15), and 165 (86).

Reaction of 3,5,7-*Trimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium-2-olate* (**3b**) *with Diphenylcyclopropenone.*—A mixture of 3,5,7-trimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-olate (**3b**) (300 mg, 1.68 mmol) and diphenylcyclopropenone (380 mg, 1.85 mmol) in toluene (30 ml) was heated under reflux for 72 h. The mixture was cooled, evaporated under reduced pressure, and the residue chromatographed on silica gel using dichloromethane–methanol (99:1) as eluant. The product was recrystallized from ethyl acetate–hexane (1:4) to give 2-[*N*-(4,6-dimethylpyrimidin-2-yl)-*N*-methylamino]-4,5-diphenyl-1,3-oxazin-6-one (**12b**) as colourless needles (230 mg, 36%), m.p. 184—186 °C (decomp.) (Found: C, 71.8; H, 5.35; N, 14.5. $C_{23}H_{20}N_4O_2$ requires C, 71.85; H, 5.25; N, 14.6%); $\nu_{max.}$(Nujol) 1 730 cm^{-1} (C=O); δ_H(CD_2Cl_2) 2.49 (s, 6 H, 4-CH_3 and 6-CH_3), 3.69 (s, 3 H, NCH_3), 6.90 (s, 1 H, 5-H), and 7.13—7.41 (m, 10 H, ArH); *m/z* (%) 384 (M^+, 38), 356 (16), 253 (97), 252 (97), 192 (100), 190 (20), 165 (89), 166 (16), 137 (37), 136 (21), and 108 (42).

Reaction of 2-[N-(4,6-*Dimethylpyrimidin-2-yl*)-N-*methylamino*]-4,5-*diphenyl*-1,3-*oxazin*-6-*one* (**12b**) *with Ammonia.*—Ammonia gas was bubbled through a stirred suspension of 2-[*N*-(4,6-dimethylpyrimidin-2-yl)-*N*-methylamino]-4,5-diphenyl-1,3-oxazin-6-one (**12b**) (95 mg, 0.25 mmol) in methanol (5 ml) for 2 min. The resulting mixture was stirred at room temperature for 30 min and the product filtered off. Recrystallization of the product from methanol gave 2-[*N*-(4,6-dimethylpyrimidin-2-yl)-*N*-methylamino]-5,6-diphenylpyrimidin-4-one (**13**) as fibrous white needles (80 mg, 84%), m.p. 229—231 °C (Found: M^+, 383.1720 $C_{23}H_{21}N_5O$ requires *M*, 383.1746); $\nu_{max.}$(Nujol) 3 630 (NH), 1 662 (C=O), and 695 cm^{-1}; *m/z* (%) 383 (M^+, 61), 382 (100), 178 (15), 43 (32), 42 (13), and 41 (25).

Reaction of 2-[N-(4,6-*Dimethylpyrimidin-2-yl*)-N-*methylamino*]-4,5-*diphenyl*-1,3-*oxazin*-6-*one* (**12b**) *with Sodium Methoxide.*—Sodium methoxide (0.12 g, 2.2 mmol) in methanol (1.1 ml) was added to a stirred suspension of 2-[*N*-(4,6-dimethylpyrimidin-2-yl)-*N*-methylamino]-4,5-diphenyl-1,3-oxazin-6-one (**12b**) (200 mg, 0.52 mmol) in methanol (5 ml). The solution was stirred at room temperature for 30 min. T.l.c. [SiO_2; EtOAc–hexane (1:3), u.v.] indicated complete reaction with the formation of two products at R_F 0.25 and 0.3. The solution was evaporated under reduced pressure and the residue chromatographed on silica using ethyl acetate–hexane (12:88) as eluant. The fractions containing the product corresponding to R_F 0.3 were combined and evaporated under reduced pressure. Recrystallization of the product from ethyl acetate–hexane (1:4) gave methyl (*Z*)-3-[*N*-(4,6-dimethylpyrimidin-2-yl)-*N*-methylureido]-2,3-diphenylprop-2-enoate (**14a**) as colourless needles (85 mg, 79%), m.p. 141—143 °C (Found: C, 69.2; H, 5.85; N, 13.4. $C_{24}H_{24}N_4O_3$ requires C, 69.2; H, 5.8; N, 13.45%); $\nu_{max.}$($CHCl_3$) 2 995, 2 945, 1 682 (C=O), 1 590, 1 570, 1 480, 1 432, 1 370, 1 345, 1 250, 1 170, 1 140, and 700 cm^{-1}; δ_H(CD_2Cl_2) 2.49 (s, 6 H, CH_3), 3.42 (s, 3 H, NCH_3), 3.70 (s, 3 H, CO_2CH_3), 6.55 (s, 1 H, pyrimidine-H), 7.00—7.16 (m, 10 H, ArH), and 11.45 (s, 1 H, NH); *m/z* (%) 417 (*M* + 1, 67), 416 (M^+, 19), 357 (11), 281 (19), 280 (100), 279 (32), 248 (11), 165 (10), 162 (11), 138 (80), and 137 (57).

The fractions containing the product corresponding to R_F 0.25 were combined, evaporated under reduced pressure, and the product recrystallized from ethyl acetate–hexane (1:3) to give methyl (*E*)-3-[*N*-(4,6-dimethylpyrimidin-2-yl)-*N*-methylureido]-2,3-diphenylprop-2-enoate (**14b**) as colourless plates (35 mg, 33%), m.p. 176—178 °C (Found: C, 69.1; H, 5.9; N, 13.35. $C_{24}H_{24}N_4O_3$ requires C, 69.2; H, 5.8; N, 13.45%); $\nu_{max.}$($CHCl_3$) 2 995, 2 945, 1 685 (C=O), 1 593, 1 570, 1 510, 1 432, 1 370, 1 340, 1 250, 1 170, 1 145, and 700 cm^{-1}; δ_H(CD_2Cl_2) 2.05 (s, 6 H, 2 × CH_3), 3.39 (s, 3 H, NCH_3), 3.49 (s, 3 H, CO_2CH_3), 6.52 (s, 1 H, pyrimidine-H), 7.20—7.50 (m, 10 H, ArH), and 11.75 (s, 1 H, NH); *m/z* (%) 417 (*M* + 1, 55), 416 (M^+, 14), 281 (18), 280 (95), 279 (29), 248 (11), 165 (13), 162 (11), 138 (100), 137 (69), and 108 (39).

Reaction of 3,5,7-*Trimethyl*[1,2,4]*triazolo*[1,5-a]*pyrimidinium-2-thiolate* (**3g**) *with Iodomethane.*—A solution of 3,5,7-trimethyl[1,2,4]triazolo[1,5-*a*]pyrimidinium-2-thiolate (**3g**) (0.22 g, 1.13 mmol) and iodomethane (0.24 g, 1.7 mmol) in dichloromethane (10 ml) was stirred at room temperature for 18 h. The solution was concentrated to 3 ml by distillation and the resulting slurry diluted with ether (10 ml). The product was filtered off to give 2-methylthio-3,5,7-trimethyl[1,2,4]triazolo-[1,5-*a*]pyrimidinium iodide (**16**) as a tan solid (0.3 g, 80%), m.p. 215 °C (decomp.); $\nu_{max.}$($CHCl_3$) 2 940, 1 640, 1 568, 1 430, and 660 cm^{-1}; δ_H($CDCl_3$) 2.82 (s, 3 H, SCH_3), 2.92 (s, 3 H, 5-CH_3), 2.95 (br s, 3 H, 7-CH_3), 3.91 (s, 3 H, NCH_3), 7.72 (s, 1 H, 6-H); *m/z* (f.a.b.) 209 (*M* − I); *m/z* (%) 208 (*M* − HI, 12), 195 (15), 194 (82), 142 (100), 141 (12), 128 (53), and 107 (20).

Acknowledgements

We thank Dr. D. J. Kennedy and Mr. P. V. Byway for the determination of n.m.r. spectra and mass spectra.

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Received 30*th November* 1988; *Paper* 8/04742A