Furazans and Furazan Oxides. Part VI.[1] New Furazano[3,4-*d*]pyrimidine *N*-Oxides: Preparation and Structure

By **Remus Nuțiu** and **A. John Boulton,*** School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ

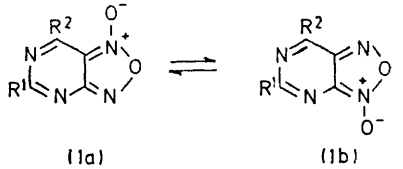
Some new furazano[3,4-*d*]pyrimidine *N*-oxides have been prepared. The tautomerism of the furazan oxide ring favours 1-oxide structures. to the virtual exclusion of the 3-oxides. Some tetrazolopyrimidine intermediates underwent hydrolytic cleavage of the pyrimidine ring, leading to tetrazole derivatives.

A NUMBER of examples of the furazano[3,4-*d*]pyrimidine † *N*-oxide (pyrimidofuroxan) system (1) have been reported.[2,3] All carry electron-donor substituents in the pyrimidine ring, and these are apparently required for stability, since the efforts of ourselves and others [2] to obtain derivatives of (1) with simple alkyl or halogen substituents have been unrewarded. The majority of the cases studied are in fact fused aminopyrimidine, pyrimidinone, or uracil derivatives, (1; $R^2 = NH_2$), (2), and (3), respectively.

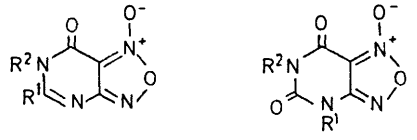
We embarked upon the present study for two reasons. First, we sought evidence for the separate existence of isomers a and b,‡ since corresponding forms can be detected at low temperature in the n.m.r. spectra of furazano[3,4-*b*]pyridine *N*-oxides.[4] The rates of interconversion of isomers can be used to provide a *qualitative* estimate of the aromaticity associated with the ring to which the furoxan system is fused,[1] and it was of interest to obtain such information for the pyrimidine, pyrimidin-4-one, and pyrimidine-2,4-dione (uracil) systems. Secondly, both furazano[3,4-*d*]pyrimidines and their *N*-oxides have been reported to be of synthetic utility,[5,6] and there seemed to be scope for further development in this area.

Pyrimidine Derivatives (1); *Ring Cleavage Reactions.*—Azidodechlorination was unsuccessfully attempted with the three chloronitropyrimidines (4)—(6); the chlorine was, however, displaced by hydrazine, giving the corresponding hydrazinopyrimidines (7)—(9). The dimethoxy and methoxy-methyl compounds (7) and (8) gave unstable azides (10) and (11) (and/or their corresponding tetrazolopyrimidine cyclised forms [2]) with nitrous acid; these were decomposed without isolation to form the corresponding furoxan derivatives (1; $R^1 = R^2 = OMe$) and (1; $R^1 = Me$, $R^2 = OMe$), respectively.

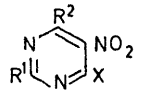
A by-product from the preparation of (1; $R^1 = Me$, $R^2 = OMe$) is the tetrazole (12), which had earlier been isolated by Temple *et al.*[2] from the reaction of 6-chloro-5-nitropyrimidin-4-one with sodium azide in aqueous acid medium. When the hydrazine (9) was nitrosated, the sole product isolated was again a tetrazole. From the high carbonyl frequency (1 745 cm^{-1}) of the acetyl group, we prefer the structure (13), rather than the isomeric formula with the acetyl group on the enamine nitrogen. β-Nitro-enamines have been isolated from nucleophilic nitropyrimidine ring-cleavage by Clark *et al.*[7]



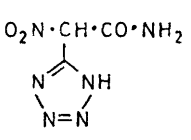
(1a) (1b)



(2) (3)



(4) $R^1 = R^2 = OMe$, X = Cl
(5) $R^1 = Me$, $R^2 = OMe$, X = Cl
(6) $R^1 = R^2 = Me$, X = Cl
(7) $R^1 = R^2 = OMe$, $X = NH \cdot NH_2$
(8) $R^1 = Me$, $R^2 = OMe$, $X = NH \cdot NH_2$
(9) $R^1 = R^2 = Me$, $X = NH \cdot NH_2$
(10) $R^1 = R^2 = OMe$, $X = N_3$
(11) $R^1 = Me$, $R^2 = OMe$, $X = N_3$



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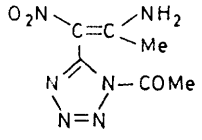


(13)

The ^1H n.m.r. spectra of the methoxy-compounds (1; $R^1 = R^2 = OMe$) and (1; $R^1 = Me$, $R^2 = OMe$) showed that in each case one of the two possible forms (1a and b) is strongly favoured, and this is assumed by analogy with earlier work [4] to be the one (1a) in which the *N*-oxide group is conjugated with the pyrimidine nitrogen atoms, rather than the non-conjugated alternative (1b). In the case of the dimethoxyfurazano-[3,4-*d*]pyrimidine *N*-oxide only two peaks, of equal

† *Chemical Abstracts* would name the ring system of (1) as [1,2,5]oxadiazolo[3,4-*d*]pyrimidine.

‡ Throughout this paper, the 1-oxides will be denoted as isomers a, the 3-oxides as b. When no distinction is intended between the isomers, the designations are omitted.

[1] Part V, A. J. Boulton and D. Middleton, *J. Org. Chem.*, 1974, **39**, 2956.
[2] C. Temple, C. L. Kussner, and J. A. Montgomery, *J. Org. Chem.*, 1968, **33**, 2086.
[3] F. Yoneda and Y. Sakuma, *J. Heterocyclic Chem.*, 1973, **10**, 993.
[4] A. J. Boulton, P. J. Halls, and A. R. Katritzky, *J. Chem. Soc.* (*B*), 1970, 636.
[5] E. C. Taylor, Y. Maki, and A. McKillop, *J. Org. Chem.*, 1972, **37**, 1601.
[6] F. Yoneda, Y. Sakuma, and S. Matsumoto, *Heterocycles*, 1975, **3**, 113.
[7] J. Clark, I. Gelling, I. W. Southon, and M. S. Morton, *J. Chem. Soc.* (*C*), 1970, 494.

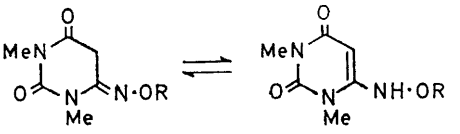
intensity, were seen, both at normal (+38 °C) and at low (−60 and −80 °C, in $CDCl_3$–$CFCl_3$) temperatures. The 7-methoxy-5-methyl compound (1; R^1 = Me, R^2 = OMe) likewise showed only two peaks at normal temperatures, but on cooling two additional very weak signals appeared, each to low field of one of the major peaks; these are attributed to *ca.* 1% of the minor tautomer (1b). At −28 °C, the chemical shifts were δ 4.25 and 2.675 for (1a), and 4.305 and 2.70 for (1b) (R^1 = Me, R^2 = OMe; methoxy and methyl groups, respectively). Coalescence, defined by the disappearance of the minor peak, occurred at *ca.* +5 (OMe) and 0 °C (CMe). Although an accurate study of the interconversion rate [(1a) ⇌ (1b)] is outside the scope of this work, qualitatively, at 0 °C the lifetime of the minor tautomer (1b) is similar to that of one of the (degenerate) tautomers of benzofuroxan.[8] The effect of the *N*-oxide group on the chemical shift of the 7-methoxy group is a shielding one: the methoxy-signal of (1a) is 0.055 p.p.m. upfield of that of (1b). Earlier work has shown methyl groups and protons to be shielded similarly (by 0.01—0.03.[4] and 0.19—0.35 p.p.m.,[9] respectively).

Uracil Derivatives (3).—The dimethyl compound (3; R^1 = R^2 = Me) was reported by Yoneda *et al.*[3,10] to be formed by the action of either sodium *nitrite* in acetic acid, or potassium *nitrate* in acetic and sulphuric acids, on 6-hydroxyamino-1,3-dimethyluracil (14), in yields of 65 and 60%, respectively. Our experience is sufficiently divergent to warrant mention. The 'hydroxylamine (14)' exists exclusively, so far as can be judged, by i.r. and n.m.r. in [$^2H_6$]acetone, in the oxime form (15). When treated with $NaNO_2$–AcOH it gave a mixture of the furoxan (3; R^1 = R^2 = Me) (40%) and the corresponding furazan (16) (25%), with a certain amount of unidentified material, m.p. 180°, of high molecular weight (by mass spectrometry). When the oxime acetate (17) reacted with sodium nitrite in aqueous hydrochloric acid, the furoxan (3; R^1 = R^2 = Me) (30%) was the only product isolated, while with sodium nitrite in acetic acid the furazan (16) was formed in good yield.

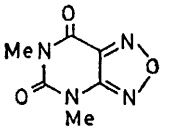
The monomethyl compound (3; R^1 = H, R^2 = Me) was reported by Yoneda *et al.*[10] as melting above 300°, and to be formed from the corresponding hydroxylamine using the nitrative cyclisation method (KNO_3–AcOH–H_2SO_4) as described above for (14). We have prepared this furoxan by another route [thermal decomposition of the tetrazolopyrimidine (18)], and find that its m.p. is 211—212°. The product was characterised by analytical and mass spectral data, and by its conversion into (3; R^1 = R^2 = Me). We therefore consider that the work of Yoneda *et al.*[10] is in error on this point.[11]

The thermal decomposition of the tetrazolopyrimidine (18) hydrate was studied by differential thermogravimetric analysis. Loss of water, and then of nitrogen, was observed. Calculation by the method of Freeman and Carroll[12] gave an estimate of 115—120 kJ mol^{-1} for the activation energy of the latter process.

We attempted to convert the furoxan ring of the uracil derivatives (3; R^1 = H or Me, R^2 = Me) into a hydroxyimidazole *N*-oxide by base-catalysed condensation with a nitroalkane, in the manner previously described for benzofuroxans.[13] However, no reaction was observed between nitromethane or 2-nitropropane and either of these fused furoxans.



(15) R = H
(17) R = Ac
(14) R = H



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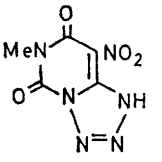

(18)

The monomethyl compound (3; R^1 = H, R^2 = Me) could be converted into a variety of 4-substituted derivatives (see Table) by alkylation under basic conditions. Some of these derivatives hold promise for the synthesis of further fused heterocyclic systems, by reductive cleavage of the furoxan ring and cyclisation of the residue at the pyrimidine 6-position to the substituent R^1; this is under investigation.

The insolubility of the 4,6-dimethyl compound (3; R^1 = R^2 = Me) at low temperatures in suitable solvents precluded the use of the n.m.r. method for investigating its tautomerism. The 4-n-butyl analogue (3; R^1 = Bu^n, R^2 = Me) was freely soluble in $CDCl_3$, but the spectrum at −28 °C was essentially identical with that at +38 °C; no new peaks were discerned above the noise level at high amplification, and it is clear that at low temperatures there prevails a single isomer, which, on the same grounds of precedent as applied above,[4,14] we expect to be the 1-oxide (3a). It is noteworthy that the dimethyl compound (3; R^1 = R^2 = Me) is suggested[6] to enter into reaction with aniline in its tautomeric form (3b). This postulate, though plausible, is, we feel, unnecessary to explain the observed results.

EXPERIMENTAL

I.r. spectra were taken on a Perkin-Elmer 257 grating spectrophotometer, and were of KBr disc preparations, unless otherwise specified. N.m.r. spectra at other than

[8] K.-I. Dahlqvist and S. Forsen, *J. Magnetic Resonance*, 1970, **2**, 61.
[9] A. J. Boulton, A. R. Katritzky, M. J. Sewell, and B. Wallis, *J. Chem. Soc.* (*B*), 1967, 914.
[10] F. Yoneda, Y. Sakuma, and M. Ueno, *J. Heterocyclic Chem.*, 1973, **10**, 415.
[11] F. Yoneda (personal communication) concurs with this conclusion.
[12] E. S. Freeman and B. Carroll, *J. Phys. Chem.*, 1958, **62**, 394.
[13] M. J. Abu-el-Haj, *J. Org. Chem.*, 1972, **37**, 2519; D. W. S. Latham, O. Meth-Cohn, and H. Suschitzky, *J.C.S. Chem. Comm.*, 1972, 1040.
[14] J. Ackrell and A. J. Boulton, *J.C.S. Perkin I*, 1973, 351; A. Gasco and A. J. Boulton, *J.C.S. Perkin II*, 1973, 1613.

normal temperatures (38 °C) were measured with a Varian HA-100 instrument, with V4343 variable temperature probe attachment; otherwise, a Perkin-Elmer R12 instrument was used. A Unicam SP 800 spectrophotometer provided the u.v. spectra. Mass spectra (70 eV ionising potential), recorded with a Hitachi–Perkin-Elmer RMU 21 instrument, were measured and were in agreement with assigned structures for all compounds named in main headings below.

Light petroleum refers to the fraction b.p. 60—80 °C.

5,7-Dimethoxyfurazano[3,4-d]*pyrimidine 1-Oxide* (1; $R^1 = R^2 = OMe$).—Nitric acid (*d* 1.56; 3 ml) was added dropwise, with cooling and stirring, to 4-chloro-2,6-dimethoxypyrimidine [15] (2.0 g) in sulphuric acid (3 ml). The mixture was warmed to 80—90 °C for 2.5 h, with continuous stirring, and was then cooled and poured onto crushed ice (50 g). The *nitropyrimidine* (4) was filtered off, washed with water, and recrystallised from ethanol, giving needles (1.7 g, 70%), m.p. 67—69°, soluble in CCl_4, C_6H_6, and $CHCl_3$ (Found: C, 32.6; H, 2.9; N, 18.9. $C_6H_6ClN_3O_4$ requires C, 32.8; H, 2.7; N, 19.4%), $\lambda_{max.}$ (MeOH) 337 (ε 1 900), 265 (16 800), and 216 nm (28 000).

The nitropyrimidine (4) (2.2 g) in methanol (50 ml) was added with stirring to hydrazine hydrate (1 g) in methanol (50 ml) at 30 °C. After 2 h the yellow solid which separated was collected by filtration, washed with water, methanol, and diethyl ether, and dried *in vacuo* (P_2O_5). The *hydrazine* (7) formed small prisms (2.0 g, 97%), m.p. 155—156° (decomp.), from tetrahydrofuran, dioxan, or a large volume of methanol, but it was sufficiently pure to be used as prepared (Found: C, 33.2; H, 4.4; N, 32.4. $C_6H_9N_5O_4$ requires C, 33.5; H, 4.2; N, 32.6%).

Aqueous sodium nitrite (1.5 g in 12 ml) was added to a stirred suspension of the hydrazine (7) (2.5 g) in hydrochloric acid (0.5M; 40 ml) at 0 °C. (Ethanol was added to reduce foaming.) The mixture was stirred at 20 °C for 2 h. The solid, which was filtered off and washed with water, a little methanol, and then ether, showed i.r. bands at 2 150 cm^{-1} [N_3 of azide (10)], and elsewhere others corresponding to the furoxan (1; $R^1 = R^2 = OMe$). This mixture was refluxed 3 h in tetrahydrofuran, the solvent was removed, and the residue was recrystallised from ethanol, giving the *furoxan* (1; $R^1 = R^2 = OMe$) as pale yellow plates or prisms (1.6 g, 70%), m.p. 166—168° (Found: C, 36.7; H, 3.2; N, 28.4. $C_6H_6N_4O_4$ requires C, 36.4; H, 3.0; N, 28.3%); $\lambda_{max.}$ (MeOH) 345 (6 350), 290 (21 000), 281 (21 200), and 215 nm (ε 31 500); $\nu_{max.}$ 1 630s, 1 560s, 1 530s, 1 340s, 1 245m, 1 210m, 1 170w, 1 075m, and 1 010m cm^{-1}; δ($CDCl_3$) 4.12 and 4.22 (OCH_3).

7-Methoxy-5-methylfurazano[3,4-d]*pyrimidine 1-Oxide* (1; $R^1 = Me$, $R^2 = OMe$).—4-Chloro-6-methoxy-2-methyl-5-nitropyrimidine [16] (5) (3.05 g) was treated with an excess of hydrazine as described for compound (4). The solid which was precipitated proved to be a mixture of the required monopyrimidylhydrazine (8) and the correspondingly disubstituted hydrazine. They were separated by sublimation at 125—130° and 0.3 mmHg, the more volatile sublimate forming orange-yellow needles of the *hydrazine* (5) (1.6 g, 53%), m.p. 137—139° (Found: C, 36.1; H, 4.6; N, 35.8. $C_6H_9N_5O_3$ requires C, 36.2; H, 4.5; N, 35.2%). The less volatile residue was recrystallised from tetrahydrofuran–light petroleum and sublimed at 180° and 0.3 mmHg, giving yellow needles of *1,2-bis-(6-methoxy-2-methyl-5-nitropyrimidin-4-yl)hydrazine*, m.p. 205—206° (Found: C, 39.2; H, 4.0; N, 30.9. $C_{12}H_{14}N_8O_6$ requires C, 39.3; H, 3.8; N, 30.6%), M^+ 366.

Aqueous sodium nitrite (0.6 g in 4 ml) was added with stirring to the hydrazine (5) (1.0 g) in hydrochloric acid (0.5M; 16 ml) at 0 °C. The mixture was stirred at 0 °C for 40 min, then for 30 min at 20 °C. It was again cooled to 0 °C and filtered. The solid, which was separated from the filtrate (A), washed with water, and dried (P_2O_5), showed an azide i.r. band (2 150 cm^{-1}). It could not be purified, but was heated to reflux (3 h) in tetrahydrofuran (60 ml). After concentration to 20 ml, hot light petroleum (120 ml) was added, and after cooling a yellow precipitate was removed. This was dissolved in acetone (25 ml) and further light petroleum (120 ml) was added. An unidentified yellow material separated. The light-petroleum-containing mother liquors were combined and evaporated to dryness, and the residue of the *furoxan* (1; $R^1 = Me$, $R^2 = OMe$) was recrystallised from water–ethanol (1 : 1), giving yellow plates (0.5 g, 55%), m.p. 109—110°, soluble in acetone, chloroform, and ethanol (Found: C, 39.9; H, 3.5; N, 30.4. $C_6H_6N_4O_3$ requires C, 39.6; H, 3.3; N, 30.8%), M^+ 182; $\lambda_{max.}$ (MeOH) 350 (2 800), 283 (3 450), 245 (5 600), and 210 nm (ε 10 800); $\nu_{max.}$ 1 630br,s, 1 580s, 1 545br,s, 1 510m, 1 465m, 1 450m, 1 430m, 1 400s, 1 375s, 1 310s, 1 300s, 1 225s, and 1 180m cm^{-1}; δ($CDCl_3$) 2.62 (CH_3) and 4.21 (OCH_3).

The filtrate (A) was concentrated to 15 ml and cooled in ice. Plates of the tetrazole (12) (0.06 g, 7%) separated and were filtered off and dried (P_2O_5); m.p. 187—189° (explosive decomp.) (lit.,[2] 192—195°); $\nu_{max.}$ 3 410s, 3 300m, 3 250br,m, 3 000vbr,m, 1 620s, 1 580s, 1 530m, 1 480s, 1 400m, 1 380w, and 1 350br,s cm^{-1}; *m/e* 172 (12%, M^+), 69, 57, 55, 44, 43 (base), 42, 30, 29, and 28.

6-Hydrazino-2,4-dimethyl-5-nitropyrimidine (9).—6-Chloro-2,4-dimethyl-5-nitropyrimidine [17] (1.4 g) in methanol (30 ml) was added with stirring to hydrazine hydrate (0.73 g) in methanol (30 ml). After 1 h stirring and a further 3 h at 20 °C the methanol was evaporated off and the residue was washed with water (20 ml) and recrystallised from CCl_4, giving the *pyrimidine* (9) as yellow needles (1.0 g, 75%) (Found: C, 39.3; H, 4.9; N, 38.3. $C_6H_9N_5O_2$ requires C, 39.3; H, 5.0; N, 38.3%).

1-Acetyl-5-(2-amino-1-nitroprop-1-enyl)tetrazole (13).—Aqueous sodium nitrite (0.42 g in 3 ml) was added dropwise to a cooled (−10 °C) stirred solution of the hydrazine (6) (0.6 g) in hydrochloric acid (0.5M; 12 ml). After 30 min stirring the cooling bath was removed and stirring was continued for 30 min at 20 °C. The mixture was again cooled, to 0 °C, and a pale yellow solid was separated by filtration, washed with cold water, and crystallised from acetone–light petroleum. The *enamino-tetrazole* (13) formed yellow needles (0.4 g, 58%), m.p. 144° (decomp.) (Found: C, 34.0; H, 3.95; N, 40.0. $C_6H_8N_6O_3$ requires C, 34.0; H, 3.8; N, 39.6%); $\lambda_{max.}$ (H_2O) 341 (7 650) and 208 nm (ε 11 400); $\nu_{max.}$ 3 240m, 3 060br,m, 1 745s, 1 620s, 1 555s, 1 505w, 1 440s, 1 400s, 1 385s, 1 370m, 1 345m, 1 285s, 1 235m, 1 180s, 1 140m, 1 070m, 1 005m, and 995m cm^{-1}; δ[$(CD_3)_2SO$] 2.13 (3 H), 2.25 (3 H), and 7.25br (2 H); *m/e* 212 (10%, M^+), 170, 153, 85, 67, 43 (base), 42, 41, and 30.

4,6-Dimethylfurazano[3,4-d]*pyrimidine-5,7(4H,6H)-dione 1-Oxide* (3; $R^1 = R^2 = Me$).—*Method* (*a*). 6-Hydroxyamino-1,3-dimethyluracil (15), prepared according to

[15] H. J. Fisher and T. B. Johnson, *J. Amer. Chem. Soc.*, 1932, **54**, 727.

[16] R. Urban and O. Schnider, *Helv. Chim. Acta*, 1958, **41**, 1806.

[17] F. L. Rose, *J. Chem. Soc.*, 1954, 4116.

Pfleiderer and Ferch,[18] had m.p. 146—148° (lit.,[18] 146—148°); δ[$(CD_3)_2CO$] 3.15 (3 H), 3.21 (3 H), 3.75 (2 H), and 9.55 (1 H). Acetylation (Ac_2O) gave the oxime acetate (17) as white needles, m.p. 129—130° (lit.,[18] 126—128°); δ($CDCl_3$) 2.16 (3 H), 3.25 (3 H), 3.48 (3 H), and 3.83 (2 H); $\nu_{max.}$ 1 770, 1 736, 1 686, and 1 620 cm^{-1}.

The oxime acetate (17) (0.6 g) was dissolved in hydrochloric acid (0.5M; 8 ml), with cautious heating (<50°). The solution was cooled to 0 °C and aqueous sodium nitrite (0.56 g in 6 ml) was added dropwise, with stirring. The mixture was then stirred at 20 °C for 3 h. The solid which separated was filtered off, washed with water, and recrystallised from ethanol, giving platelets or needles, m.p. 245° (decomp.) [lit.,[3] 245° (decomp.)] (0.16 g, 28%). The product was occasionally discoloured yellow or pink, but without affecting the m.p. or i.r. spectrum. Although the yield was not high, the product was uncontaminated with the furazan (16).

Method (*b*). The oxime (15) (0.85 g) was treated with aqueous sodium nitrite and hydrochloric acid, following Yoneda and Sakuma's [3] Method A. The yellow solid product was separated (t.l.c.) into three components: the furoxan (3; $R^1 = R^2 = Me$) (0.4 g, 40%), the furazan (16) (0.2 g, 25%), m.p. 225—226° (lit.,[5] 225—226°), and an unidentified solid (0.05 g), m.p. 180°.

When the oxime acetate (17) (0.6 g) in acetic acid (1.5 ml) and water (10 ml) was treated dropwise with aqueous sodium nitrite (0.56 g in 6.7 ml) at 0 °C, then stirred for 1 h at 20 °C, the brown mixture deposited a white crystalline solid, which formed plates (from ethanol or acetone) of the furazan (16) (0.47 g, 90%), m.p. 225—226°, identical with that obtained in method (*b*).

6-*Methyl*-8-*nitrotetrazolo*[1,5-c]*pyrimidine*-5,7(1H,6H)-*dione* (18).—1-Methylbarbituric acid [19] was converted into 4-chloro-1-methyluracil,[20] which was then nitrated,[21] giving 4-chloro-1-methyl-5-nitrouracil [' 6-chloro-2-hydroxy-3-methyl-5-nitro-4(3*H*)-pyrimidinone ' [21]]. The nitrouracil (2.05 g) was refluxed (7 h) with sodium azide (1.0 g) in tetrahydrofuran (100 ml). After cooling, the solid was filtered off and washed with tetrahydrofuran (some nitrouracil was recovered from the solvent). The remaining solid was soluble in methanol, being precipitated by addition of benzene. The material showed an azide i.r. band (2 140 cm^{-1}), but it appeared to isomerise readily to the *tetrazolopyrimidine* (18), a process which was hastened by stirring with hydrochloric acid (2N; 25 ml). The white solid so obtained (1.7 g, 75%) was soluble in acetone, from which it was precipitated by light petroleum. The tetrazolopyrimidine formed needles of a monohydrate, which could be dehydrated (3 h; 70° and 0.1 mmHg). It decomposes at *ca.* 155°, and then melts 190—192° [Found (anhydrous material): C, 28.15; H, 1.8; N, 39.2. $C_5H_4N_6O_4$ requires C, 28.3; H, 1.9; N, 39.6%]; $\lambda_{max.}$ (0.1N-HCl) 341 (ε 15 750) and 265sh nm (4 100); $\nu_{max.}$ (of hydrate) 3 530m, 3 420m, 1 745s, 1 680s, 1 635s, 1 505w, 1 460s, 1 380w, 1 340m, 1 315m, 1 250m, 1 190w, 1 035m, and 980m cm^{-1}.

6-*Methylfurazano*[3,4-d]*pyrimidine*-5,7(4H,6H)-*dione* 1-*Oxide* (3; $R^1 = H$, $R^2 = Me$).—The tetrazolopyrimidine (18) (1.15 g) was heated for 18 h at 120° and 0.3 mmHg. The residue was recrystallised from acetone–light petroleum (1 : 1), and then from carbon tetrachloride, giving white platelets of the *furoxan* (0.78 g, 85%), m.p. 211—212° (decomp.) (Found: C, 32.6; H, 2.2; N, 30.4. $C_5H_4N_4O_4$ requires C, 32.6; H, 2.2; N, 30.4%); $\lambda_{max.}$ (dioxan) 312 (ε 1 700) and 267.5 nm (11 400); $\nu_{max.}$ 3 160w, 3 040w, 1 730m, 1 700s, 1 650s, 1 600w, 1 545w, 1 445m, 1 380w, 1 335m, 1 275m, and 1 205m cm^{-1}.

N(4)-Alkylation of 6-methylfurazano[3,4-*d*]pyrimidine-5,7(4*H*,6*H*)-dione 1-oxide (3; $R^1 = H$, $R^2 = Me$)

	Product (3; R^1 = as indicated, R^2 = Me) [a]			
Halide R^1X	M.p. (°C)	Yield (%)	Recryst. solvent; form	$\lambda_{max.}$/nm (ε) (in MeOH)
MeI	245 [b]	70	95% EtOH–H_2O; plates	317 (1 550), 268 (11 350) [c]
EtI	172—173	40	H_2O; platelets	317 [d] (1 200), 269 (9 750)
Bu^nI	104—105	55	50% EtOH–H_2O; platelets	317 [d] (1 550), 269 (12 300)
$H_2C{:}CH{\cdot}CH_2Br$	88—90	45	H_2O; plates	315 (1 200), 268.5 (8 400)
$MeCO{\cdot}CH_2Br$	117—118 [e]	30	H_2O; needles	315 (1 200), 267 (10 100)
$PhCO{\cdot}CH_2Br$	210—211	50	95% EtOH–H_2O; needles	322 (2 600), 265 [d] (12 850), 248 (17 500)

[a] All new compounds gave satisfactory analytical (C, H, N), i.r., and mass spectral data. Analytical data are available as Supplementary Publication No. SUP 21744 (2 pp.); for details of Supplementary Publications see Notice to Authors No. 7 (*J.C.S. Perkin I*, 1975, Index issue). [b] Lit.,[3] 245°. [c] In ethanol; from ref. 3. [d] Inflection. [e] Softens and partly decomposes *ca.* 109°.

Thermal decomposition of the tetrazolopyrimidine (18) could also be effected (75% yield) by reflux for 3 h in glacial acetic acid. The synthesis of (3; $R^1 = H$, $R^2 = Me$) was also achieved (66% yield from the chloronitrouracil) without purification of the intermediate (18).

Attempts to effect condensation of the furoxans (3; $R^1 = H$ or Me, $R^2 = Me$) with nitromethane or 2-nitropropane, in tetrahydrofuran, pyridine, or dimethylformamide, in the presence of triethylamine, gave no recognisable products, with in most cases recovery of the furoxan in good yield. The tetrahydrofuran solutions from the reactions with the monomethyl furoxan deposited large yellow prisms, m.p. 96—97°, recrystallisable from carbon tetrachloride (as needles), which were formed also in the absence of the nitroalkane, and proved to be the *triethylammonium salt* of the furoxan (3; $R^1 = H$, $R^2 = Me$) (Found: C, 46.5; H, 6.7; N, 24.5. $C_{11}H_{19}N_5O_4$ requires C, 46.5; H, 6.3; N, 24.1%).

N(4)-*Alkylation of* 6-*Methylfurazano*[3,4-d]*pyrimidine*-5,7(4H, 6H)-*dione* 1-*Oxide*.—The following general procedure was used to obtain the products detailed in the Table. The furazanopyrimidine oxide (3; $R^1 = H$, $R^2 = Me$) (0.46 g) in dry dimethylformamide (DMF) (25 ml) was treated with lithium hydride (0.02 g).[22] The solution was stirred at 70 °C while the halide was dropped in over 10—15 min (in DMF solution if a solid). After further stirring at 70 °C for 1.5 h, the solvent was removed *in vacuo* and the residual syrup was triturated with water (20 ml). The

[18] W. Pfleiderer and H. Ferch, *Annalen*, 1958, **615**, 52.
[19] H. Blitz and H. Wittek, *Ber.*, 1921, **54**, 1035.
[20] G. Nübel and W. Pfleiderer, *Chem. Ber.*, 1962, **95**, 1613.
[21] G. D. Davies, R. K. Robins, and C. C. Cheng, *J. Amer. Chem. Soc.*, 1962, **84**, 1724.
[22] *Cf.* J. A. Vida, *Tetrahedron Letters*, 1972, 3921. Other bases were not tried; there is no reason to suppose they would be less successful.

solid so obtained was filtered off and recrystallised as indicated. Purity of recrystallised materials was checked by t.l.c.

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