min. The metal shreds were thoroughly washed with water and then transferred to a stirred solution of 15.1 g (21.4 mmol) of **18R** in 200 mL of THF and 50 mL of water. Detosylation took place at ambient temperature, the progress being monitored by HPLC analysis. After complete conversion (usually requiring 2–4 h), the gray suspension was filtered through Celite and concentrated in vacuo. The residue was distributed between ice-cold ether/THF (100 mL, 30 mL) and 4 N NaOH (25 mL), and the organic layer was extracted again with 1 N NaOH (30 mL) and water (30 mL) and finally was shaken with 50 mL of 1 N aqueous NH_4I. Evaporation of the etheral phase left a residue, which was crystallized from toluene/ether at low temperature to give 12.3 g (85%) of $4{\cdot}I^-$.

(2*S*,8*R*)-2-[[(*tert*-Butyldimethylsilyl)oxy]methyl]-8-[[(*tert*-butyldiphenylsilyl)oxy]methyl]-3,4,6,7,8,9-hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine Hydroiodide ($4{\cdot}I^-$): mp 128 °C; HPLC (85% CH_3OH) R_v = 10.4 mL; (80% CH_3OH) R_v = 17.2 mL; ^1H NMR (360 MHz, $CDCl_3$) δ 8.95 (br s, ≈1 H, NH), 8.81 (br s, ≈1 H, NH), 7.56 (m, 4 H, arom H), 7.36 (m, 6 H, arom H), 3.76 (dd, J = 3.8/10.0 Hz, 1 H, CHO), 3.70 (dd, J = 7.8/13.9 Hz 1 H, CHO), 3.55 (m, 1 H, H-2*), 3.45 (m, 3 H, CHO, H-8*), 3.25 (m, 1 H, H-4*), 3.12 (3 H, H-4* and H-6*), 2.02–1.78 (m, 4 H, H-3 and H-7), 1.06 (s, ≈9 H, *tert*-butyl CH_3), 0.85 (s, ≈9 H, *tert*-butyl CH_3), 0.05 (s, ≈3 H, $SiCH_3$), 0.03 (s, ≈3 H, $SiCH_3$); ^{13}C NMR (90.5 MHz, $CDCl_3$) δ 151.6 (C-10), 135.6, 135.5, 132.7, 130.0, 127.9 (arom C), 65.2, 64.9 (CO), 49.2, 49.0 (C-2, C-8), 45.1, 44.6 (C-4, C-6), 26.9, 25.8 (*tert*-butyl CH_3), 23.1, 22.8 (C-3, C-7), 19.2, 18.1 (*tert*-butyl CSi), −5.41, −5.47 ($SiCH_3$); MS m/z (% I) 552 (51, guanidine cation, M^+), 406 (82, $M^+ - CH_3OSi(CH_3)_2C_4H_9$), 284 (100, $M^+ - CH_3OSi(C_6H_5)_2C_4H_9$). Anal. Calcd for $C_{31}H_{50}N_3O_2Si_2I$ (679.8): C, 54.77; H, 7.41; N, 6.18. Found: C, 54.90; H, 7.34; N, 6.13.

Acknowledgment. We appreciate the competent technical assistance of Mrs. Ch. Strobel and Ms. H. Oswald. This work was supported by Deutsche Forschungsgemeinschaft and Fonds der Chem. Industrie. We gratefully acknowledge a generous gift of chiral starting materials by Degussa AG, Hanau.

Tetrazolo[1,5-*a*]pyridines and Furazano[4,5-*b*]pyridine 1-Oxides

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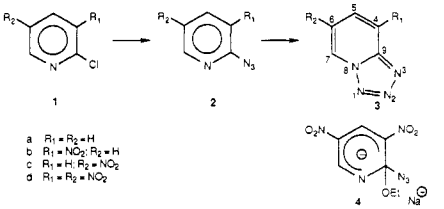
Tetrazolo[1,5-*a*]pyridines may be prepared by the reaction of azide ion with 2-chloropyridines. These tetrazolo[1,5-*a*]pyridines are shown to be in equilibrium with the corresponding 2-azidopyridines. Furazano[4,5-*b*]pyridine 1-oxides may be prepared by thermolysis of the appropriate 4-nitrotetrazolo[1,2-*a*]pyridines, presumably via the corresponding 2-azido-3-nitropyridines. The furazano[4,5-*b*]pyridine 1-oxides are found to be in equilibrium with the 3-oxides. ^1H and ^{13}C NMR are used to examine this equilibrium.

Introduction

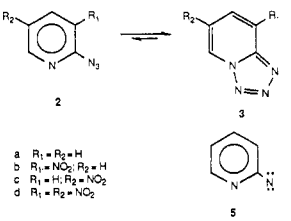
Benzofuroxans (2,1,3-benzoxadiazole 1-oxides) have shown interesting chemistry and wide ranging biological activity.[1] Vasodilatory activity,[2] inhibition of nucleic acid and protein synthesis in leucocytes,[3] and activity against leukemia[4] have all been observed. Benzofuroxan derivatives have also found use as depolarizing agents in dry cell batteries,[5] as polymerization inhibitors,[6] and in pest control.[7] Our interest in these compounds, however, has been as energetic materials, where our goals are improved performance and decreased sensitivity to such environmental stimuli as heat, impact, and friction.

Benzofuroxans have been prepared by oxidation of *o*-quinone dioxime[8] or by oxidation of *o*-nitroanilines with alkaline hypochlorite[9] or (diacetoxyiodo)benzene.[10] Perhaps the most satisfactory method, however, has been the thermolysis of *o*-nitrophenyl azides.[11] A recent report has described a one-pot synthesis of benzofuroxans from *o*-chloronitrobenzenes, involving nucleophilic displacement of the chlorine by azide ion followed by in situ cyclization under solid–liquid phase-transfer catalysis conditions.[12]

Scheme I



Scheme II



(1) Gasco, A.; Boulton, A. J. *Adv. Heterocycl. Chem.* **1981**, *29*, 252. Ghosh, P. B.; Ternai, B.; Whitehouse, M. W. *Med. Res. Rev.* **1981**, *2*, 158.
(2) Ghosh, P. B.; Everitt, B. J. *J. Med. Chem.* **1974**, *17*, 203.
(3) Ghosh, P. B.; Whitehouse, M. W. *J. Med. Chem.* **1968**, *11*, 305.
(4) Ghosh, P. B.; Whitehouse, M. W. *J. Med. Chem.* **1969**, *12*, 505.
(5) Hardy, W. B.; Parent, R. A. French Patent 1 395 886, 1965, American Cyanamid Co.; *Chem. Abstr.* **1965**, *63*, 14875.
(6) Shimazu, H.; Arai, T.; Harada, S. *Japan Kokai* 102231, 133931; *Chem. Abstr.* **1978**, *88*, 62733, 90234.
(7) Iwamoto, R.; Sakata, H.; Okumura, K.; Honga, A. Japan Patent 77 07 055, 1977, Nitto Chemical Industry Co. Ltd.; *Chem. Abstr.* **1977**, *87*, 12883d.
(8) Zincke, T.; Schwarz, P. *Ann. Chem.* **1899**, *28*, 307.
(9) Green, A. G.; Rowe, F. M. *J. Chem. Soc.* **1912**, *101*, 2443.
(10) Boulton, A. J. Middleton, D. *J. Org. Chem.* **1974**, *39*, 2956.
(11) Smith, P. A. S.; Brown, B. B. *J. Am. Chem. Soc.* **1951**, *73*, 2435.

(Investigations in these laboratories suggest that phase-transfer catalysis may be unnecessary.[13]) As an extension of our interest in benzofuroxans, we chose to examine the synthesis and chemistry of tetrazolo[1,5-*a*]pyridines and furazano[4,5-*b*]pyridine 1-oxides (pyridofuroxans).

Results and Discussion

Synthesis of Tetrazolo[1,5-*a*]pyridines and Equilibria with 2-Azidopyridines. 2-Chloropyridines have been shown to react with sodium azide in the presence of hydrochloric acid to give the corresponding tetrazolo[1,5-*a*]pyridines.[14] The reaction, of course, proceeds by initial nucleophilic displacement of chlorine by the azide ion, followed by an electrocyclic ring closure (Scheme I). Predictably, the presence of an electron-withdrawing nitro group at the 3- or 5-position aids the initial displacement, and whereas the reaction of 2-chloropyridine (1a) itself must be carried out in DMF under reflux, the corresponding reactions of 3- and 5-nitro-2-chloropyridines **1b,c** proceed smoothly and in high yield in refluxing ethanol. Indeed, 2-chloro-3,5-dinitropyridine (**1d**) reacts with hydrazoic acid in ethanol at ambient temperature. (In the absence of acid, **1d** reacts with sodium azide in ethanol to form the Meisenheimer-type complex **4**, which is converted to the desired product by treatment with hydrochloric acid in ethanol.)

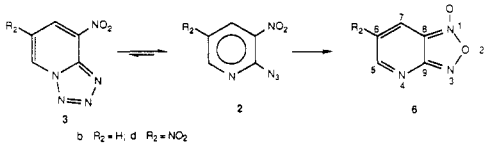
However the presence of the nitro groups also affects the cyclization to form the tetrazolopyridine. The azidopyridine and the tetrazolopyridine are in equilibrium (Scheme II). In the case of the unsubstituted compound, the equilibrium is far to the right. No trace of the azido compound **2a** can be detected in the infrared or NMR spectra, although the loss of 28 mass units provides the base peak of the mass spectrum and the generation of the pyridine-2-nitrene (**5**) has been cited in the pyrolysis of tetrazolopyridine.[15] Similarly 4-nitrotetrazolo[1,5-*a*]pyridine (**3b**) appears to be free of the azido isomer **2b**, with no trace of the latter being visible in the infrared and NMR spectra. Once again, however, the mass spectrum of **3b** showed a prominent peak at 137 attributed to the loss of molecular nitrogen. On the other hand, the NMR spectrum of 6-nitrotetrazolo[1,5-*a*]pyridine (**3c**) in acetone-d_6 showed the presence of the azido compound **2c** at the level of 10%. Even more pronounced, the product from the reaction of hydrazoic acid with 2-chloro-3,5-dinitropyridine (**1d**), when dissolved in acetone-d_6, contains a mixture of two compounds identified as 4,6-dinitrotetrazolo[1,5-*b*]pyridine (**3d**) (60%) and the azido isomer **2d** (40%). These results have been conveniently explained in terms of the electron-withdrawing nitro groups at the 4- and 6-positions destabilizing the electronegative tetrazole ring in favor of the azido group. The failure to detect any evidence for **2b** would appear to be anomalous.

The presence of the azidopyridine **2d**, in association with the tetrazolopyridine **3d**, in acetone solution was confirmed by Fourier-transform infrared spectroscopy (FTIR), which showed an azido absorption (doublet) at 2153 and 2143 cm^{-1} as well as three nitro-group bands at 1599, 1575, and 1553 cm^{-1}. The FTIR spectrum of a standard pressed KBr disk of the solid showed only two nitro group bands, at 1575 and 1553 cm^{-1}, and no obvious azido band. However, diffuse reflectance FTIR spectroscopy, followed by careful reexamination of the standard spectrum confirmed that the azido isomer is indeed present in the solid state, at least in small quantities. In view of the simultaneous presence of the two forms in solution, it comes as no surprise that the material is extremely difficult to recrystallize. The best purification appears to be dissolution in aqueous ethanol, followed by evaporation of the ethanol at ambient temperature under high vacuum.

Table I. Equilibrium between 4,6-Dinitrotetrazolo[1,5-*a*]pyridine and 2-Azido-3,5-dinitropyridine in Various Solvents

solvent	2-azido-3,5-dinitropyridine present, %
$CDCl_3$	100
C_6D_6	80
$(CD_3)_2CO$	40
CD_3CN	37.5
$(CD_3)_2SO$	9

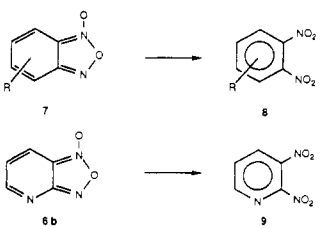
Scheme III



The equilibrium between the two forms in solution is markedly affected by the solvent, as illustrated in Table I. Thus in chloroform-*d* the azido form **2d** is present at 100% to the exclusion of **3d**, while in DMSO-d_6 **2d** is present to only 9%, the tetrazolopyridine dominating at 91%.

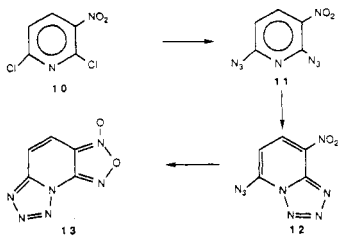
Synthesis of Furazano[4,5-*b*]pyridine 1-Oxides. The equilibrium between 4,6-dinitrotetrazolo[1,5-*a*]-pyridine and 2-azido-3,5-dinitropyridine is further complicated by the fact that 2-azido-3,5-dinitropyridine undergoes reaction in solution at ambient temperature. The nature of the reaction in acetone- and DMSO-d_6 is still uncertain, but in chloroform-*d*, benzene-d_6, and acetonitrile-d_3 the azido compound loses molecular nitrogen and recyclizes to form 6-nitrofurazano[4,5-*b*]pyridine 1-oxide (6-nitropyridofuroxan) (**6d**) (Scheme III). The half-life for this reaction is ca. 3 days in chloroform or benzene and ca. 16 days in acetonitrile at room temperature. The process is thermal, occuring equally rapidly in the dark. The same conversion may be achieved by cautiously heating **2d**/**3d** alone to 120 °C, or more conveniently by heating in toluene for 30 min in the dark under reflux until the gas evolution is completed. In a similar fashion the parent furazano[4,5-*b*]pyridine 1-oxide (pyridofuroxan) (**6b**) may be prepared by heating a toluene solution of **3b** under reflux, providing some evidence that the latter compound is also in equilibrium with the corresponding azido isomer, at least at elevated temperatures.

Benzofuroxans (benzofurazan 1-oxides) (**7**) may be oxidized to substituted 1,2-dinitrobenzenes **8** by the action of 90% hydrogen peroxide in sulfuric or polyphosphoric acid, although the oxidation of benzodifuroxans is less successful.[16] It was hoped that application of a similar procedure might provide access to 2,3-dinitropyridines.

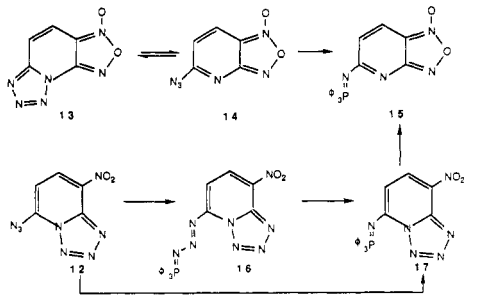


(12) Ayyangar, N. R.; Madan Kumar, S.; Srinivasan, Z. V.; *Synthesis* **1987**, 616.
(13) Norris, W. P. To be published.
(14) Boyer, J. H.; McCane, D. I.; McCarville, W. J.; Tweedie, A. T. *J. Am. Chem. Soc.* **1953**, *75*, 5298.
(15) Wentrup, C. *Tetrahedron* **1970**, *26*, 4969.
(16) Boyer, J. H.; Huang, C. *Chem. Commun.* **1981**, 365; *Heterocycles* **1982**, *19*, 285.

Scheme IV



Scheme V



The pyridofuroxans proved to be more resistant to oxidation by reagents ranging in strength from chloroperbenzoic acid to peroxydisulfuric acid in 30% oleum. In no case could any sign of pyridine *N*-oxide be detected, but the furoxan ring of **6b** was oxidized by peroxydisulfuric acid formed in situ from 90% hydrogen peroxide in 30% oleum, giving the previously unknown 2,3-dinitropyridine (**9**). However 6-nitrofurazano[4,5-*b*]pyridine 1-oxide (**6d**) appears to be stable toward oxidation even under these conditions. This is a rather disappointing result, but the oxidation of **6d** will be investigated further.

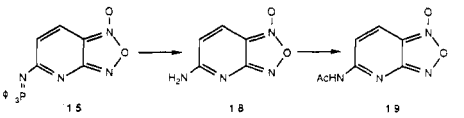
Tetrazolo[1,5-*f*]furazano[4,5-*b*]pyridine 1-Oxide. If the presence of nitro groups at the 4- and 6-positions destabilizes the tetrazolo[1,5-*a*]pyridine ring system with respect to the 2-azidopyridine, it seemed reasonable that a furoxan ring fused at the 6- and 7-positions might stabilize it. Taking advantage of the formation of both tetrazolo- and furazanopyridines described above, 3-nitro-2,6-dichloropyridine (**10**) was treated with excess sodium azide. In this case the best reaction medium seemed to be acetonitrile rather than acidic aqueous ethanol. If the reaction was carried out under reflux conditions, tetrazolo[1,5-*f*]furazano[4,5-*b*]pyridine 1-oxide (furoxanotetrazolopyridine) (**13**) was obtained directly. If the reaction was carried out at ambient temperature, an azidotetrazolo[1,5-*a*]pyridine was isolated, contaminated with about 10% of **13** (Scheme IV). The azido compound was characterized by IR and NMR spectroscopy, and the structure **12** (presumably being formed via the intermediate **11**) was proposed on the basis of the slightly greater stability, at least in acetone solution, of 2-nitrotetrazolo[1,5-*a*]pyridine (**3b**) than the 6-nitro isomer **3c** with respect to the azido tautomers **2b** and **2c**, respectively, as discussed above. Reaction of **10** with 1 equiv of azide, carried out in an effort to identify whether the 2-chloro or 6-chloro group is displaced first, gave a 50:50 mixture of the azido compound **12** and the unreacted starting material, with no trace of a monochloro intermediate being detected. Clearly, the first azido group (or tetrazolo functionality) strongly activates the remaining chloro group to displacement. Thermolysis of **12** results in the formation of **13**, and this route probably affords the most efficient synthesis of this compound.

The structure **12** for the intermediate azidotetrazolo[1,5-*a*]pyridine was supported by analysis of the reaction

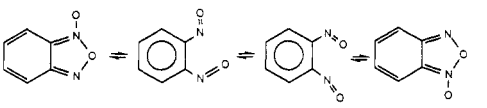
Table II. Equilibrium between Tetrazolo[1,5-*f*]furazano[4,5-*b*]pyridine 1-Oxide (13) and Azidofuroxanopyridine 14 in Various Solvents

solvent	azidofuroxanopyridine present, %
$CDCl_3$	39
C_6D_6	15
CD_3CN	6
$(CD_3)_2CO$	0
$(CD_3)_2SO$	0

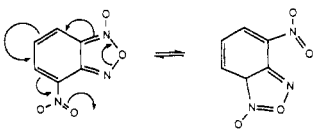
Scheme VI



Scheme VII



Scheme VIII



of **12** and **13** with triphenylphosphine.[17] The furoxanotetrazolopyridine **13** reacts with triphenylphosphine in ethanol under reflux to form the phosphinimine **15**, perhaps through the intermediacy of the azidofuroxanopyridine **14** (Scheme V). When **12** was treated with triphenylphosphine in ethanol at ambient temperature, conditions selected to avoid equilibrium with the diazido compound **11**, an orange precipitate was produced. This material was identified as the Staudinger intermediate **16**, which proved to be thermally unstable, however, decomposing with the evolution of nitrogen when heated in ethanol under reflux to give the phosphinimine **17**, a yellow solid. This material was also formed by the reaction of **12** with triphenylphosphine in benzene solution at ambient temperature. Heating **17**, or indeed **16**, in toluene under reflux afforded the phosphinimine **15**, thus establishing the structure of **12**. Since **13** can form only one phosphinimine, and the same material may be derived from **12** using these mild conditions under which rearrangement is improbable, the position of the azido group must be that shown in **12**. However, it must be noted that the thermal instability and insolubility of both **16** and **17** made purification of these compounds impossible, while their NMR and mass spectra are somewhat equivocal.

In view of the equilibrium already observed between the tetrazolopyridines and the isomeric 2-azidopyridines, and the reaction of **13** with triphenylphosphine to give **15**, a reexamination of the NMR spectrum of the tetrazolofuroxanopyridine **13** in various solvents seemed warranted. The results of this investigation are included in Table II and confirm a similar equilibrium between **13** and the azidofuroxanopyridine **14** in such solvents as acetonitrile, benzene, and chloroform. However, the portion of azido compound present is markedly less than that in the case of 4,6-dinitrotetrazolo[1,5-*a*]pyridine (**2d**), as shown in Table I, and the furoxan ring clearly does stabilize the tetrazolopyridine ring system.

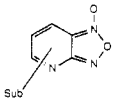
Note that acid-catalyzed hydrolysis of the phosphinimine **15** yielded 5-aminofurazano[4,5-*b*]pyridine 1-oxide

(17) VanAllan, J. A.; Reynolds, G. A. *J. Heterocycl. Chem.* **1968**, *19*, 471.

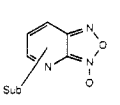
(18). This product was characterized as the acetyl derivative **19** (Scheme VI). and should provide access to further nitrogen-substituted pyridofuroxans. This possibility will be examined further in a subsequent publication.

Tautomerism of Pyridofuroxans. Benzofuroxans exhibit a particularly rich and diverse chemistry, and notable within that chemistry is their propensity for tautomerism, with the exocyclic oxygen migrating between the 1- and 3-positions. Two different modes of rearrangement have been identified. In the first (Scheme VII) the furoxan ring undergoes electrocyclic ring-opening to an intermediate dinitrosobenzene, which rearranges before recyclizing in the opposite sense.[18] The second mode of rearrangement (Scheme VIII) is restricted to 4-nitrobenzofuroxans and occurs by a more extensive electrocyclic rearrangement involving both the furoxan ring and the nitro group.[19] These reactions have manifested themselves both in dynamic equilibria between two positional isomers and in the initial formation of kinetically favored isolable products and their subsequent rearrangement to the thermodynamically favored isomer.

In light of the rearrangements in the benzofuroxan series, the structure of the pyridofuroxans warrants further examination. These materials are obtained as pure single compounds, with no trace of the alternative isomer being detected in either the final product or the reaction mixture. The 1-oxide structures **6b**, **6d**, **13**, **15**, **18**, and **19** were assigned initially on the basis of the azido compounds from which they are ultimately derived. Intuitively, they would also appear to be the energetically more probable structures, but the alternative 3-oxide structures **6b′**, **6d′**, **13′**, **15′**, **18′**, and **19′** must be considered.



6b,d, 13, 15, 18, 19



6b,d', 13', 15', 18', 19'

It is not readily apparent how to distinguish chemically between the 1-oxide and 3-oxide isomers. However ^{13}C NMR offers a possible solution to this problem. In a ^{13}C NMR study involving a series of some 15 benzofuroxans, C_8 has a chemical shift of 115 ± 5 ppm, while C_9 has a chemical shift of 150 ± 5 ppm.[20] Assuming that the furoxan chemical shift increments for the benzenoid series can also be applied for the pyridofuroxans, the C_8 and C_9 chemical shifts for furazano[4,5-*b*]pyridine 1-oxides should be about 110 and 170 ppm, while those for the 3-oxides should be about 144 and 136 ppm, respectively. The observed ^{13}C NMR data for **6b**, **6d**, **13**, **18**, and **19** are given in Table III. Putting aside for a moment **13**, which can be expected to be significantly perturbed by the fuzed tetrazole ring, the mean chemical shifts for the bridge carbons are about 108 and 159 ppm, strongly implicating the proposed 1-oxide structure. However, in the case of the parent pyridofuroxan **6b** and the nitro derivative **6d**, these signals were very broad. An obvious explanation for this broadness is that the peaks represent the weighted average of two tautomers exchanging at an "intermediate" rate, the position of the peaks indicating that the 1-oxide structures are strongly favored. Support for this argument was gained by examination of the ^{13}C NMR spectra at −25 °C, whereupon small additional peaks attributable to the methine carbons of the alternative 3-oxide structures became visible. The signals due to the bridge carbons C_8 and C_9 were not discernible, however. This result was confirmed by variable-temperature ^1H NMR spectroscopy. In the case of **6b**, the ^1H NMR at −25 °C showed a sharp and distinguishable component, present at ca. 10%, and identified as **6b′**. At 10 °C this had collapsed to three broadened singlets, while at 45 °C it had sharpened up again to show considerable fine structure. The situation was not quite so clear for **6d** due to the similarities in chemical shifts. However at −20 °C, signals due to **6d** were discernible to about 8%. At 23 °C the spectrum had coalesced to two broader singlets; at 45 °C it had sharpened again to a clean AB pattern. Thus, the indications are that there is an equilibrium between the 1-oxide and the 3-oxide tautomers for the pyridofuroxans **6b** and **6d**, but that the 1-oxide structure is strongly favored.

This variation of ^{13}C and ^1H NMR spectra was not observed in the case of **13**, **18**, and **19**. In each case the ^{13}C NMR showed sharp signals for the bridge protons, while neither the ^{13}C nor the ^1H NMR gave any indication of signals due to a second tautomer. This could be because the equilibrium is rapid compared with the NMR time scale even at low temperatures, or, more likely, because the 1-oxide is so strongly favored over the 3-oxide. Strong support for this hypothesis was gained by single-crystal X-ray structure determination on the tetrazolo[1,5-*f*]furazano[4,5-*b*]pyridine 1-oxide (**13**). Unfortunately suitable crystals of the other pyridofuroxans could not be prepared, but in **13** the exocyclic oxygen is clearly located on N_1. (This structure is illustrated in Figure 1, in which the atoms are labeled for crystallographic convenience rather than by IUPAC rules. Thus N_1 becomes N(2). This numbering system is used throughout the following discussion of the single-crystal X-ray structure results and in the table of atomic coordinates.)

In addition to locating the position of the exocyclic oxygen, the structure determination showed, as expected, that **13** is approximately planar. The pyridofuroxan

Table III. ^{13}C NMR Chemical Shifts (ppm) of Pyridofuroxans

		chemical shift		
compd	carbon no.	calculated	ambient	−25 °C
6b	9	160.4	160 (br)	160.44
	8	109.4	110 (br)	109.59
	7	123.2	123.92	123.32, 127.76[a]
	6	125.9	126.39	125.80, 129.23[a]
	5	161.6	160.88	161.68, 157.28[a]
6d	9	159.5	159 (br)	159.51
	8	108.8	109 (br)	109.03
	7	123.4	123.67	123.43, 122.32[a]
	6	143.6	144.11	143.53
	5	155.4	154.91	155.65, 150.42[a]
13	10	137.6	146.86	
	9	103.5	109.09	
	8	120.6	120.61	
	7	118.5	117.56	
	12	161.4	152.01	
18	9	160.7	160.03	
	8	99.9	106.23	
	7	124.5	121.84	
	6	113.5	121.58	
	5	180.8	161.97	
19	9	160.6	158.01	
	8	103.8	107.15	
	7	124.3	124.43	
	6	116.0	120.57	
	5	172.7	158.01	
	CO		170.78	
	CH_3		24.44	

[a] Signals attributed to 3-oxide tautomer.

(18) Katritzky, A. R. *Rec. Chem. Prog.* **1962**, *23*, 223.
(19) Boulton, A. J.; Katritzky, A. R. *Proc. Chem. Soc.* **1962**, 257.
(20) Anet, F. A. L.; Yavari, I. *Org. Magn. Reson.* **1976**, *8*, 158. Witanowski, M.; Stefaniak, L.; Biernat, S.; Webb, G. A. *Org. Magn. Reson.* **1980**, *14*, 365. Chafin, A. P.; Moore, D. W. To be published.

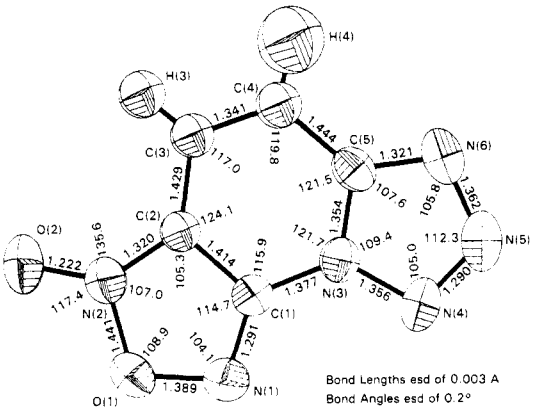


Figure 1. Single-crystal X-ray structure of tetrazolo[1,5-*f*]furazano[4,5-*b*]pyridine 1-oxide (**13**).

portion (C(1) through C(5), N(1) through N(3), O(1) and O(2)) is planar within the expected standard deviations. The plane of the tetrazole ring (C(5) and N(3) through N(6)) deviates from the plane of the pyridofuroxan moiety by an angle of 1°. The bond lengths of the furoxan portion of the molecule are within three estimated standard deviations or less of the mean bond lengths for furoxans.[21] The pyridine ring has a distinct variation of long and short bonds, reflecting the influence of the tetrazole and furoxan functionalities. The C(1)–N(3) and C(5)–N(3) bonds are both longer (1.377 (2) and 1.354 (3) Å, respectively) than the reported mean of 1.337 (12) Å for pyridine C–N bonds. The C(2)–C(3) and C(4)–C(5) bonds are both long (1.429 (3) and 1.444 (3) Å), whereas, the C(3)–C(4) bond is short (1.341 (3) Å) compared with the aromatic C–C bond length of 1.380 (15) Å found in other pyridines. The latter reference does not report mean bond lengths for tetrazoles. However, the bond lengths in the tetrazole portion of **13** are the same as those found in two similar compounds (namely, 7-nitro-5,6,7*H*-imidazolo[1,2-*d*]tetrazole and bistetrazolo[1,5-*a*:1′,5′-*c*]pyrazine), within the estimated standard deviations.[22]

Conclusion

Tetrazolo[1,5-*a*]pyridines may be prepared by reaction of azide ion with 2-chloropyridines and are found to be in equilibrium in solution with the intermediate 2-azidopyridines. The position of this equilibrium is found to vary with the solvent. The presence of electron-withdrawing nitro groups at the 3- and 5-positions facilitates displacement of the chlorine, but it also destabilizes the tetrazolopyridine with respect to the azido–pyridine tautomer. Furazano[4,5-*b*]pyridine 1-oxides may be obtained by thermolysis of 4-nitrotetrazolo[1,5-*a*]pyridines. They are found to be in equilibrium with the tautomeric furazano[4,5-*b*]pyridine 3-oxides in solution, at least in some cases, but the equilibrium strongly favors the 1-oxide.

Experimental Section

Melting points were determined in capillary tubes on a Buchi 510 melting point apparatus. More detailed thermal behavior was determined on a Dupont 1090 thermal analyzer. Infrared spectra were determined in KBr disks using a Perkin-Elmer Model 1330 spectrophotometer, while FTIR spectra were recorded on a Nicolet 60SX instrument. ^{1}H NMR spectra were determined in acetone-d_6 solutions (unless stated otherwise) using an IBM NR-80 instrument; ^{13}C NMR spectra were recorded on the same instrument operating at 20 MHz or on a Nicolet NT-200 instrument operating at 50 MHz. Mass spectra were determined on a Perkin-Elmer 5985 GC/MS. High resolution mass spectra (HRMS) were determined on a Kratos 902/50 instrument. *WARNING: Many of the compounds described in this report are explosives which may be subject to accidental initiation by such stimuli as friction, heat, and impact. Appropriate precautions should therefore be taken in their handling and/or use.*

Tetrazolo[1,5-*a*]pyridine (3a). 2-Chloropyridine (**1a**) (3.00 g, 26.4 mmol) and sodium azide (2.00 g, 30.7 mmol) were heated in DMF (50 mL) at 130–140 °C for 48 h. The solvent was removed by evaporation under reduced pressure, and the residue was recrystallized from ethanol (with decolorization) to give tetrazolo[1,5-*a*]pyridine (**3a**) as buff-colored crystals (0.61 g; 21%), mp 154–6 °C (lit.[14] mp 156–8 °C). (This purification process appears to be both wasteful and inefficient.) IR: 1630, 1490, 1100, 770, 755 cm^{-1}. ^{1}H NMR: δ 7.47 (H_6), 7.85 (H_5), 8.10 (H_4), 9.12 (H_7) [$J_{4,5}$ = 8.95 Hz; $J_{4,6}$ = 1.30 Hz; $J_{4,7}$ = 0.88 Hz; $J_{5,6}$ = 6.52 Hz; $J_{5,7}$ = 3.08 Hz; $J_{6,7}$ = 6.78 Hz]. ^{13}C NMR: δ 116.19 (C_4), 117.73 (C_6), 126.89 (C_7), 133.30 (C_5), 149.52 (C_9). MS, *m/z* 120 (parent ion), 92 (base peak).

4-Nitrotetrazolo[1,5-*a*]pyridine (3b). 2-Chloro-3-nitropyridine (**1b**) (0.50 g, 3.2 mmol) and sodium azide (0.50 g, 7.7 mmol) were dissolved in 10% aqueous ethanol (50 mL) at ambient temperature, and 10% hydrochloric acid (5 mL) was added. The solution was then heated under reflux for 48 h. Evaporation to dryness, addition of water (ca. 10 mL), and filtration gave a buff solid residue (0.45 g, 86%). Recrystallization from ethanol gave **3b** as tan needles (0.27 g), mp 171–3 °C dec (lit.[14] mp 167–8 °C). IR: 1635, 1545, 1520, 1490, 1345, 1320, 820, 795, 760 cm^{-1}. ^{1}H NMR: δ 7.74 (H_6), 8.88 (H_5), 9.58 (H_7) [$J_{5,6}$ = 7.62 Hz, $J_{5,7}$ = 0.91 Hz, $J_{6,7}$ = 6.89 Hz]. ^{13}C NMR: δ 116.75 (C_6), 132.12 (C_5), 133.16 (C_7), 137.62 (C_4), 144.65 (C_9). MS, *m/z*: 165 (parent ion), 137, 107, 91, 77, 64 (base peak).

6-Nitrotetrazolo[1,5-*a*]pyridine (3c). 2-Chloro-5-nitropyridine (**1c**) (0.50 g, 3.2 mmol) was dissolved in 10% aqueous ethanol (50 mL), and sodium azide (0.50 g, 7.7 mmoles) in aqueous ethanol (20 mL) was added at ambient temperature. The mixture was then warmed to redissolve the reagents, 10% hydrochloric acid (5 mL) was added, and the solution was heated under reflux for 48 h. The ethanol was removed by evaporation under reduced pressure, and the solid was filtered off to give 0.33 g, 63%. Recrystallization from ethanol gave **3c** as colorless plates, mp 139–41 °C (lit.[14] mp 138–40 °C). IR: 1630, 1560, 1525, 1500, 1350, 1330, 1050, 800, 730 cm^{-1}. ^{1}H NMR: δ 8.33 (H_4), 8.58 (H_5), 10.31 (H_7) ($J_{4,5}$ = 9.82 Hz, $J_{4,7}$ = 0.94 Hz, $J_{5,7}$ = 1.94 Hz) [also contains 10% 2-azido-5-nitropyridine (**5c**), δ 7.13 (H_3), 8.57 (H_4), 9.20 (H_6) ($J_{3,4}$ = 8.90 Hz, $J_{3,6}$ = 0.65 Hz, $J_{4,6}$ = 2.93 Hz]. ^{13}C NMR: δ 116.50 (C_4), 127.29 (C_7), 127.81 (C_5), 141.28 (C_6), 150.35 (C_9), [also contains **5c** δ 114.96 (C_3), 135.35 (C_4), 143.15 (C_5), 146.13 (C_6), 160.47 (C_2)]. MS, *m/z*: 165 (parent ion and base peak).

4,6-Dinitrotetrazolo[1,5-*a*]pyridine (3d). A. 2-Chloro-3,5-dinitropyridine (**1d**) (0.10 g, 0.5 mmol) and sodium azide (0.10 g, 1.5 mmol) were dissolved in 10% aqueous ethanol (25 mL) and stirred at ambient temperature overnight. Evaporation to dryness under reduced pressure gave an orange solid mass (0.16 g), shown by ^{1}H NMR to contain the Meisenheimer complex **4**. (^{1}H NMR: δ 1.10 (t, 3 H, CH_3), 3.87 (dq, 2 H, $-OCH_2-$, shows evidence of restricted rotation), 7.14, 8.83 (AB quartet, J = 0.80 Hz, 2 H, aromatic). IR: 2110, 1590, 1550, 1280, 1230, 1220, 1060 cm^{-1}). The orange solid (0.08 g) was redissolved in 10% aqueous ethanol (25 mL), and 10% hydrochloric acid (3 mL) was added. The solution was stirred at ambient temperature overnight. Evaporation of the ethanol and filtration gave the tetrazolopyridine **3d** (0.05 g, 90%) as yellow needles.

B. 2-Chloro-3,5-dinitropyridine (**1d**) (0.50 g, 2.5 mmol) and sodium azide (0.50 g, 7.7 mmol) were dissolved in 10% aqueous ethanol (50 mL). After the addition of 10% hydrochloric acid (3 mL), the solution was stirred at ambient temperature overnight. Evaporation of the ethanol under reduced pressure gave **3d** as a pale yellow solid (0.45 g, 87%), mp 123 °C dec. The best purification procedure was redissolution in 10% aqueous ethanol, followed by evaporation of the ethanol under reduced pressure and filtration. IR: 1640, 1570, 1550, 1535, 1470, 1460, 1445, 1420, 1370, 1060, 975, 740 cm^{-1}. ^{1}H NMR: δ 9.42 (H_5), 10.81 (H_7) ($J_{5,7}$ = 1.84 Hz) [also contains 40% 2-azido-3,5-dinitropyridine (**2d**),

(21) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II*, **1987**, S1.
(22) Gilardi, R.; George, C.; Flippen-Anderson, J. L. ONR Annual Report N001485WR24060-1985A, Washington D.C. Oct 1984–Oct 1985.

δ 9.17 (H_4), 9.44 (H_6) ($J_{4,6}$ = 2.48 Hz)]. ^{13}C NMR: δ 126.54 (C_5), 132.87 (C_7), 136.06 (C_4), 139.62 (C_6), 148.86 (C_9) [also contains **5d**, δ 131.70 (C_4), 133.62 (C_3), 141.70 (C_5), 145.31 (C_6), 153.80 (C_2)]. MS, *m/z*: 210 (parent ion), 182, 152, 106, 78 (base peak)]. HRMS: $C_5H_2N_6O_4$ requires 210.0137, found 210.0139.

Furazano[4,5-*b*]pyridine 1-Oxide (6b). 4-Nitrotetrazolo-[1,5-*a*]pyridine (**3b**) (0.50 g, 3.0 mmol) was dissolved in toluene (50 mL) and heated under reflux for 4 h, or until the evolution of nitrogen was complete. The solution was decolorized with charcoal and filtered and evaporated to dryness to leave **6b** as a pale yellow solid (0.40 g, 96%). Recrystallization from cyclohexane gave pale yellow needles (0.27 g), mp 52–3 °C (lit.[14] mp 52–3 °C). IR: 1610, 1525, 1395, 1370, 1125, 1030, 800 cm^{-1}. ^1H NMR: δ 7.45 (H_6), 8.05 (H_7), 8.86 (H_5) ($J_{5,6}$ = 3.76 Hz, $J_{5,7}$ = 1.65 Hz, $J_{6,7}$ = 9.08 Hz). ^{13}C NMR: δ 109.42 (C_8), 123.23 (C_7), 125.89 (C_6), 160.43 (C_9), 161.60 (C_5). MS, *m/z*: 137 (parent ion), 107, 77, 76, 52 (base peak), 50.

6-Nitrofurazano[4,5-*b*]pyridine 1-Oxide (6d). A. 4,6-Dinitrotetrazolo[1,5-*a*]pyridine (**3d**) (0.10 g, 0.5 mmol) was placed in a test tube and carefully heated in an oil bath to ca. 120–130 °C. The pale yellow tetrazole melted suddenly with the evolution of gas and yellow vapor. The residue was cooled, solidified, and sublimed to give **6d** as a yellow solid, mp 93–6 °C (lit.[12] mp 106 °C).

B. 4,6-Dinitrotetrazolo[1,5-*a*]pyridine (**3d**) (0.35 g, 1.7 mmol) was dissolved in toluene (25 mL) and heated slowly with stirring in an oil bath. At ca. 75 °C, evolution of gas commenced. The solution was heated to 95 °C until the gas evolution ceased, cooled, filtered, and then evaporated to dryness to give **6d** as a yellow solid (0.28 g, 92%). Recrystallization from benzene gave yellow crystals, mp 93–4 °C (lit.[12] mp 106 °C). IR: 1610, 1595, 1545, 1345, 1180, 825, 765 cm^{-1}. ^1H NMR: δ 9.14 (H_7), 9.51 (H_5) ($J_{5,7}$ = 2.41 Hz). ^{13}C NMR: δ 108.79 (C_8), 123.42 (C_7), 143.59 (C_6), 155.42 (C_5), 159.46 (C_9). MS, *m/z*: 182 (parent ion), 152, 106, 78 (base peak), 76, 75.

2,3-Dinitropyridine (9). Furazano[4,5-*b*]pyridine 1-oxide (**6b**) (0.13 g, 0.95 mmol) was dissolved in 30% oleum (6 mL) and cooled in an ice bath. Hydrogen peroxide (90%, 1.5 mL) was added dropwise with stirring. The solution was allowed to warm to ambient temperature, and the reaction was allowed to continue for 24 h. Quenching on ice and extraction with dichloromethane (3 × 50 mL) gave an oil (0.13 g), whose NMR indicated ca. 70% reaction. Flash chromatography (benzene/silica) gave two fractions; the first yielded a pale oil (0.08 g, 60%), triturated with hexane to give **9** as a tan solid (mp 43–5 °C). IR: 1600, 1560, 1540, 1370, 1355, 1080, 875 cm^{-1}. ^1H NMR: δ 8.16 (H_5), 8.87 (H_6), 8.92 (H_4) (the latter two assignments could possibly be reversed) ($J_{4,6}$ = 1.40 Hz; $J_{4,5}$ = 4.75 Hz; $J_{5,6}$ = 8.30 Hz). ^{13}C NMR: δ 130.24 (H_5), 137.21 (H_4), 153.94 (H_6) (the NO_2-bearing carbons C_2 and C_3 could not be reliably assigned). MS, *m/z*: 169 (parent ion), 123, 77, 76, 53 (base peak). The second fraction contained unreacted starting material (0.04 g). All attempts at oxidation of **6b** under milder conditions were unsuccessful. Attempted oxidation of **6d** under these conditions gave only general decomposition with copious evolution of gas.

Tetrazolo[1,5-*f*]furazano[4,5-*b*]pyridine 1-Oxide (13). A. 3-Nitro-2,6-dichloropyridine (**10**) (1.00, 5.2 mmol) was dissolved in acetonitrile (50 mL), and sodium azide (1.00 g, 27.8 mmol) was added. The mixture was heated under reflux with stirring for 4 h, at which time the gas evolution appeared to be complete. Filtration and evaporation gave a brown/yellow solid (0.81 g, 88%) identified as **13**.

B. 3-Nitro-2,6-dichloropyridine (**10**) (1.0 g, 5.2 mmol) was dissolved in acetonitrile (50 mL), and sodium azide (1.00 g, 27.8 mmol) was added. The mixture was stirred at ambient temperature for 24 h and then filtered and evaporated to dryness to leave a yellow/tan solid (0.97 g). This solid was dissolved in benzene (50 mL), filtered, and evaporated to give a pale yellow solid (0.93 g, 95%) identified as 7-azido-6-nitrotetrazolo[1,5-*a*]-pyridine (**12**) containing 10% of **13**, which was not further purified. IR: 2080, 2075, 2060, 1585, 1570, 1510, 1320, 1280 cm^{-1}. ^1H NMR: δ 6.86 (H_5), 7.96 (**13**), 8.48 (H_4) ($J_{4,5}$ = 8.65 Hz). MS, *m/z*: 206 (parent ion). The solid **12** (0.93 g) was redissolved in benzene (50 mL) and heated under reflux for 4 h. Filtration and evaporation to dryness left **13** as an off-white solid (0.78 g, 85% overall). Best purification is by recrystallization from benzene to give off-white crystals, mp 135.5–7 °C; sublimation gave a somewhat inferior product. IR: 1630, 1550, 1510, 1405, 800 cm^{-1}. ^1H NMR: δ 7.96 (s). ^{13}C NMR: δ 109.09 (C_9), 117.56 (C_7), 120.61 (C_8), 146.86 (C_{10}), 152.01 (C_{12}). MS, *m/z*: 178 (parent ion), 150, 120, 63 (base peak). HRMS: $C_5H_2N_6O_2$ requires 178.0239, found 178.0238.

C. 3-Nitro-2,6-dichloropyridine (**10**) (0.050 g, 2.6 mmol) was dissolved in acetonitrile (25 mL), and sodium azide (0.18 g, 2.9 mmol) was added. The reaction mixture was stirred at ambient temperature for 3 days, filtered, and evaporated to leave a tan solid (0.45 g). This solid was shown by NMR to consist of three compounds, two being **12** and **13**. Dissolution in toluene (25 mL) and heating under reflux converted **12** to **13**; flash chromatography (chloroform/silica) gave only unreacted **10** (0.20 g, 40%) and **13** (0.21 g, 46%). No trace of the monochloro intermediate was detected.

5-(Triphenylphosphoranylideneamino)furazano[4,5-*b*]-pyridine 1-Oxide (15). Tetrazolo[1,5-f]furazano[4,5-b]pyridine 1-oxide (**13**) (0.40 g, 2.3 mmol) and triphenylphosphine (0.60 g, 2.3 mmol) were added to ethanol (50 mL) and heated under reflux for 2 h until the gas evolution was complete. The mixture was cooled and allowed to stand overnight and then filtered and washed with ethanol to give **15** as a yellow solid (0.83 g, 90%), mp 228–30 °C dec. IR: 1600, 1565, 1490, 1410, 1320, 1095, 910, 685, 520 cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.00 (H_7), 7.33 (J_{P-H} = 2.55 Hz) (H_6) (the latter two assignments could possibly be reversed) (J_{6-7} = 9.30 Hz), 7.49 (m, 6 H), 7.58 (m, 3 H), 7.86 (m, 6 H). ^{13}C NMR ($CDCl_3$): δ 106.92 (C_8), 119.70 (J_{P-C} = 4.40 Hz), (C_7), 127.18 (J_{P-C} = 100.23 Hz) (phenyl C_1), 128.68 (J_{P-C} = 12.32) (phenyl $C_{2,6}$), 129.64 (J_{P-C} = 26.79 Hz) (C_6), 132.47 (J_{P-C} = 2.77 Hz) (phenyl C_4), 133.32 (J_{P-C} = 10.06 Hz) (phenyl $C_{3,5}$), 160.36 (C_9), 167.70 (J_{P-C} = 7.04 Hz) (C_5). MS, *m/z*: 412 (parent ion), 382, 262, 183 (base peak), 108. HRMS: $C_{23}H_{17}N_4O_2P$ requires 412.1089, found 412.1046.

7-[(Triphenylphosphoranylideneamino)azo]-4-nitrotetrazolo[1,5-*a*]pyridine (16). 7-Azido-4-nitrotetrazolo[1,5-*a*]pyridine (**12**) (0.44 g, 2.1 mmol) and triphenylphosphine (0.54 g, 2.1 mmol) were stirred in ethanol (25 mL) at ambient temperature for 2 h. The resultant orange solid was filtered and washed with ethanol to give **16** (0.86 g, 88%), mp 98–100 °C dec. IR: 1605, 1500, 1420, 1330, 1205, 1180, 1110, 1095, 910, 720, 690, 520 cm^{-1}. ^1H NMR: δ 6.80–8.50 (br m). MS, *m/z*: 440 (no parent ion), 412, 382, 304, 262, 183 (base peak).

7-(Triphenylphosphoranylideneamino)-4-nitrotetrazolo-[1,5-*a*]pyridine (17). A. 7-Azido-4-nitrotetrazolo[1,5-*a*]pyridine (**12**) (0.38 g, 1.8 mmol) and triphenylphosphine (0.45 g, 1.7 mmol) were dissolved in benzene (25 mL) and stirred at ambient temperature for 2 h. The resultant yellow precipitate was filtered, washed with benzene, and dried to give **17** (0.56 g, 74%), mp 180 °C dec. IR: 1600, 1570, 1500, 1420, 1190, 1135, 1100, 930, 915, 710, 690, 520 cm^{-1}. ^1H NMR: δ 6.85–8.35 (br m). MS, *m/z*: 440 (parent ion), 412, 382, 366, 304, 277, 262, 183 (base peak), 152, 108.

B. The orange powder **16** (0.40 g, 0.9 mmol) was suspended in ethanol (25 mL) and was heated under reflux with the evolution of gas. When the gas evolution ceased (ca. 2 h), the mixture was cooled, and the yellow solid was filtered, washed with ethanol, and dried to give **17** (0.34 g, 90%). The yellow solid **17** (0.20 g, 0.5 mmol) was suspended in toluene (25 mL) and was heated under reflux with the evolution of gas. When the gas evolution ceased and the solid dissolved, the solution was cooled and evaporated to half volume, whereupon a yellow crystalline solid precipitated. Filtration and recrystallization from toluene gave **15** (0.14 g, 75%), identified by IR and ^1H NMR.

5-Aminofurazano[4,5-*b*]pyridine 1-Oxide (18). 5-(Triphenylphosphoranylideneamino)furazano[4,5-*b*]pyridine 1-oxide (**17**) (1.2 g, 2.9 mmol) was suspended in glacial acetic acid (10 mL), and concentrated hydrochloric acid (5 mL) was added at ambient temperature. The solid immediately went into solution, which was stirred at ambient temperature overnight to give a white precipitate, identified as the amine hydrochloride salt. Filtration and stirring the solid in water containing an excess of potassium carbonate gave a yellow solid (0.28 g, 63%) identified as **18**. The acetic acid mother liquors were quenched with water (250 mL), filtered to remove the triphenylphosphine, and basified with potassium carbonate. Continuous extraction with dichloromethane for 3 days yielded a further 0.16 g of solid (total yield

0.44 g, 98%). Recrystallization gave **18** as yellow crystals, mp 234–6 °C dec. IR: 3360, 3110, 1670, 1620, 1600, 1510, 1480, 1235, 1120, 1015 cm^{-1}. ^1H NMR: δ 6.91 (H_6), 7.61 (H_7) ($J_{6,7}$ = 9.46 Hz). ^{13}C NMR (d_6-DMSO): δ 106.23 (C_8), 121.58 (C_6), 121.84 (C_7), 160.03 (C_9), 161.97 (C_5). MS, *m/z*: 152 (parent ion), 79 (base peak), 52. HRMS: $C_5H_4N_4O_2$ requires 152.0334, found 152.0328.

5-Acetamidofurazano[4,5-*b*]pyridine 1-Oxide (19). 5-Aminofurazano[4,5-*b*]pyridine 1-oxide (**18**) (0.10 g, 0.7 mmol) was added to glacial acetic acid (3 mL) and acetic anhydride (3 mL) and heated under reflux overnight. The solution was cooled and quenched in water (30 mL) and neutralized with potassium carbonate. Extraction with dichloromethane (3 × 25 mL) gave a pale yellow solid (0.125 g, 98%). Recrystallization from ethanol gave **19** as a pale yellow powder, mp 187–90 °C. IR: 3250, 1710, 1600, 1580, 1500, 1430, 1400, 1325, 1255, 1200, 1110, 1030, 1005, 995, 835 cm^{-1}. ^1H NMR: δ 2.31 (s, 3 H, $COCH_3$), 7.99 (H_6), 8.34 (H_7) ($J_{6,7}$ = 9.70 Hz). ^{13}C NMR (d_6-DMSO): δ 24.44 (CH_3), 107.15 (C_8), 120.57 (C_6), 124.43 (C_7), 158.01 (C_9), 170.78 (CO and C_5). MS, *m/z*: 194 (parent ion), 152, 95, 79, 64, 52, 43 (base peak). HRMS: $C_7H_6N_4O_3$ requires 194.0440, found 194.0432.

Single-Crystal X-ray Structure of Tetrazolo[1,5-*f*]furazano[4,5-*b*]pyridine 1-Oxide (13). Tetrazolo[1,5-*f*]-furazano[4,5-*b*]pyridine 1-oxide (**13**) crystallized as salmon-colored platelets from benzene in space group $P2_12_12_1$, Z = 4, D_x = 1.719. A crystal of dimensions 0.06 × 0.32 × 0.56 mm with (001) platelet faces was used for data collection on a Nicolet R3 instrument. Unit cell parameters a = 5.961 (1), b = 9.968 (2), and c = 11.589 (2) Å were determined from a least-squares fit of 25 computer-centered reflections with 2θ values ranging from 8 to 28° (Mo K_α). $2\theta/\theta$ intensity data were collected at room temperature (291 K) at variable scan speeds of 2–6°/min over a 2θ range 4–54° for octants $\bar{h}k\bar{l}$, $\bar{h}kl$, $hk\bar{l}$, hkl with monochromated Mo K_α radiation. Three check reflections (210), (01$\bar{2}$), and ($\bar{1}$41), collected every 93 reflections, were constant. All data reduction and structure solution/refinement calculations were performed with SHELXTL.[23] The 3311 observations were corrected for Lorentz and polarization effects. Because of the crystal shape, numerical Gaussian absorption corrections (μ = 1.31 cm^{-1}) were applied; minimum and maximum transmission factors were 0.957 and 0.991, respectively. Equivalent reflections were merged (R_{merge} = 0.0106) to yield 1511 unique data of which 1370 with $|F_o| > 4\sigma(F)$ were used in refinement. With the inclusion of four additional reflections in the starting set, the positions of all C, N, O atoms were observed on the first E_{map} obtained by direct, multisolution methods. All N, O atoms and C(1), C(5) were refined anisotropically; C(2), C(3), C(4) were refined isotropically. The two H atoms were refined as "riding" on their adjacent carbon atoms but with unconstrained isotropic thermal parameters. The 105 parameters were refined with the blocked cascade algorithm of SHELXTL[23] and with weights $w = 1/[\sigma^2(F) + 0.0009F^2]$. Maximum shift/esd ratios were less than 0.05 for the final refinement cycles. Final agreement factors were R = 0.040, R_w = 0.054, goodness of fit = 1.39, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - F_c|)^2/\sum(|F_o|)^2]^{1/2}$. Final difference Fourier maps had peaks and troughs ranging from +0.40 to 0.28 $e^-/Å^3$. Crystallographic data, including final atomic coordinates, have been deposited.

(23) SHELXTL, version 4.1, Nicolet XRD (1984).

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths and angles, and anisotropic thermal parameters for **13** (3 pages); observed and calculated structure factors for **13** (9 pages). Ordering information is given on any current masthead page.

Reaction of 4,4-Diethyl-3,5-pyrazolidinedione with Carboxylic Acid Anhydrides. N-Acylation vs O-Acylation

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The acylation of 4,4-diethyl-3,5-pyrazolidinedione with carboxylic acid anhydrides was investigated in order to establish the position(s) of acylation on the pyrazolidine ring. The reaction was carried out with acetic, propanoic, butanoic, pentanoic, chloroacetic, and benzoic anhydrides. Both a monoacylated and a diacylated product were isolated in each case. IR, UV, ^1H and ^{13}C NMR, and mass spectroscopic data were not diagnostic of the structures. X-ray crystallography showed that the products were N-acylated and N,N-diacylated compounds, respectively. No N,O-diacylated products were obtained. ^{15}N NMR spectroscopy appears to be a useful spectroscopic technique for establishing the position(s) of acylation.

Several reports of acylation reactions between 3,5-pyrazolidinediones and carboxylic acid anhydrides or acid chlorides yielding monoacylated and/or diacylated products have been published.[1-8] The published results are conflicting in that the products have been reported to be both N-acylated derivatives **2** and **3**[1-6] and O-acylated derivatives **2A** and **3A**.[7,8] No example of an N,O-diacylated derivative **4** has been reported. The assignments of the

(1) Godin, J.; Le Berre, A. *Bull. Soc. Chim. Fr.* **1968**, *10*, 4210.
(2) Dormoy, M.; Godwin, J.; Le Berre, A. *Bull. Soc. Chim. Fr.* **1968**, *10*, 4222.
(3) Zinner, G.; Moll, R.; Boelke, B. *Arch. Pharm.* **1966**, *299*, 441.
(4) Nasr, H.; El-Zanfally, S.; Khalifa, M.; Abu-Shady, H. *Pharmazie* **1976**, *31*, 7745.
(5) Nasr, H.; El-Zanfally, S.; Khalifa, M. *Egypt. J. Pharm. Sci.* **1976**, *15*, 345.
(6) Kornet, M. J.; Thorstenson, J. H.; Lubawy, W. C. *J. Pharm. Sci.* **1974**, *63*, 1090.
(7) Ruhkopf, H. *Chem. Ber.* **1940**, *73B*, 820.
(8) Gillis, B. T.; Izydore, R. A. *J. Org. Chem.* **1969**, *34*, 3181.

0022-3263/90/1955-3761$02.50/0