Cyclisation Reactions of some 3-Nitrosoimidazo[1,2-*a*]-pyridines and -pyrimidines. Ring-opening/Ring-closure Reactions with Triethyl Phosphite: Reassignment by *X*-Ray Crystal Structure and Nuclear Magnetic Resonance

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Deoxygenation of 3-nitroso-2-phenylimidazo[1,2-*a*]-pyridines and -pyrimidines with triethyl phosphite does not lead to the products described in the literature as pyrido- and pyrimido-imidazoindoles (3) and (4), but to the open-chain derivatives, *N*-(2-pyridyl)- and *N*-(2-pyrimidyl)-benzimidoyl cyanides (5) and (6). *X*-Ray crystallographic analysis confirms the structure of (5a): orthorhombic system with a = 24.377 (6), b = 11.729 (3), c = 7.534 (2) Å, space group *Pbca*, Z = 8, d = 1.27 g/cm^3, R = 0.061. Thermal ring-closure with triethyl phosphite of compounds (5) and (6) produced the 3-amino-2-phenylimidazo[1,2-*a*]-pyridines and -pyrimidines (8) and (9).

Most of the reported reactions of nitroso compounds with tervalent phosphorus reagents have involved aromatic systems.[1] Deoxygenation of *C*-nitroso derivatives by $P(OEt)_3$ is known to give the corresponding azoxy compounds; however, a more important reaction takes place, involving the reductive cyclisation of the nitroso compounds to a variety of heterocyclic systems *via* a nitrene, when an excess of reducing agent is used.[2] In this way, imidazoindole derivatives have been synthesized. This paper describes the synthesis and the revised structures of the pyrido- and pyrimido-[2′,1′: 2,3]-imidazo[4,5-*b*]indoles (3) and (4) reported in the literature.

Results and Discussion

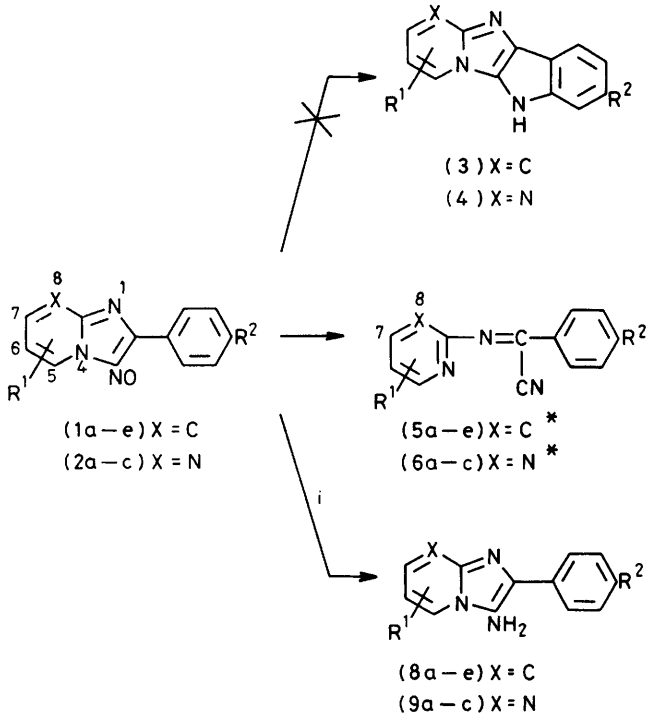
Few reactions of *C*-nitroso derivatives appear in the literature. However, it has been reported that the reaction of equimolar quantities of nitrosoimidazo-pyridine (or -pyrimidine) with triethyl phosphite in toluene gives a moderate yield of the pyrido- or pyrimido-imidazoindole together with 3-amino compounds.[3] In an attempt to achieve a more satisfactory conversion of nitroso compounds into indole derivatives, and thus reduce the possibility of the formation of by-products, the reaction was investigated using a molar excess of triethyl phosphite over the nitroso compounds, in the absence of solvent (Scheme 1). Compounds (1a—e) and (2a—c) (0.02 mol) and freshly distilled $P(OC_2H_5)_3$ (30 ml, 0.15 mol) were refluxed for 5—15 min under a flow of dry nitrogen gas. The excess of triethyl phosphite was removed by vacuum distillation and the residue chromatographed (Alumina, CH_2Cl_2 as eluant), producing, after recrystallization from CH_2Cl_2, compounds (5a—e) and (6a—c) (Table 1). Comparison of m.p., i.r. spectrum and t.l.c. with the literature showed these to be the same products as those previously obtained: (5a) and (6a) gave m.p.s 79—81 and 97—99 °C respectively, molecular formulae $C_{13}H_9N_3$ and $C_{12}H_8N_4$ (from the elemental analysis and mass spectrum), and i.r. bands at 2 550 and 1 650 cm^{-1}. However, the ^{1}H n.m.r. and ^{13}C n.m.r. assignments disagreed with the expected indole structure.[3,4]

The 250 MHz ^{1}H n.m.r. spectra, taken in $CDCl_3$, for compounds (5a—e) and (6a—c)† (Table 1) confirm this conclusion and support structures (5) and (6). Thus (5b) exhibits phenyl resonances at δ 7.07 (d, 2 H) and 8.17 (d, 2 H), signals at δ 8.57 (dd, 10-H), 7.77 (td, 8-H), and 7.20 (m, 7-, 9-H) corresponding to the expected four shielded hydrogens of the pyridine nuclei, and one at δ 3.87 (OCH). On the other hand the methoxy derivative (6b) exhibits two sharp doublets of equal intensity at δ 8.18 and 7.01, respectively, for the 2 and 2′ and 3 and 3′ phenyl protons respectively, a triplet at δ 7.21 (9-H), a doublet at δ 8.80 (8-, 10-H) and a singlet at δ 3.88 (OMe).

Analysis of the observed perturbations in the spin-decoupled 250 Mz ^{1}H n.m.r. spectrum of (5c) confirms this structure. Indeed, with irradiation at δ 7.09 (2 H), the signal at δ 8.45 (1 H) sharpens considerably. Irradiation of the corresponding coupled aromatic protons at δ 7.54 (3 H) increased the signal at δ 8.21 (2 H). Thus, eight aromatic protons were found without N–H groups. Similar results were obtained from the ^{1}H n.m.r. spectrum of the pyrimidyl analogue (6b) (Figure 1). Selective irradiation of the basic structure, (6a), at the resonance frequency of 8- and 10-H identified the signal due to 9-H as a singlet at δ 7.29. Irradiation at the frequency of 3- and 3′-H then allowed the assignment of 2- and 2′-H to the signal at δ 7.56 with subsequent simplification for 1-H at δ 7.65.

The ^{13}C n.m.r. assignments for compounds (5a—c) are given in Table 2. Interestingly, the ^{13}C n.m.r. spectrum of (5e) in $(CD_3)_2SO$ at room temperature showed the presence of one methyl and seven C(H) resonances, and six quaternary carbon signals. The largest splitting is centred at 165.35 p.p.m. and arises from one-bond coupling ($^1J_{CF}$ 253.3 Hz); the signal corresponds to C(1). The two doublets centred at 116.76 and 131.11 p.p.m. with coupling constants $^2J_{CF}$ 22.0 and $^3J_{CF}$ 10.0 Hz are assigned to C(2) and C(2′), and C(3) and C(3′), respectively. The doublet centred at 130.20 p.p.m. is assigned to the quaternary carbon C(4). Peaks at 16.70 and 111.69 p.p.m. are typical of the Me and CN carbons. The five signals corresponding to the five carbon nuclei of pyridine were

† The n.m.r. numbering for compounds (5) and (6) is shown in Table 2.



* Labels 7 and 8 in compounds (5) and (6) refer to the corresponding positions in starting compounds (1) and (2) and are not part of the numbering system used for the names.

Scheme 1. *Reagents:* i, $P(OEt)_3$, 120 °C

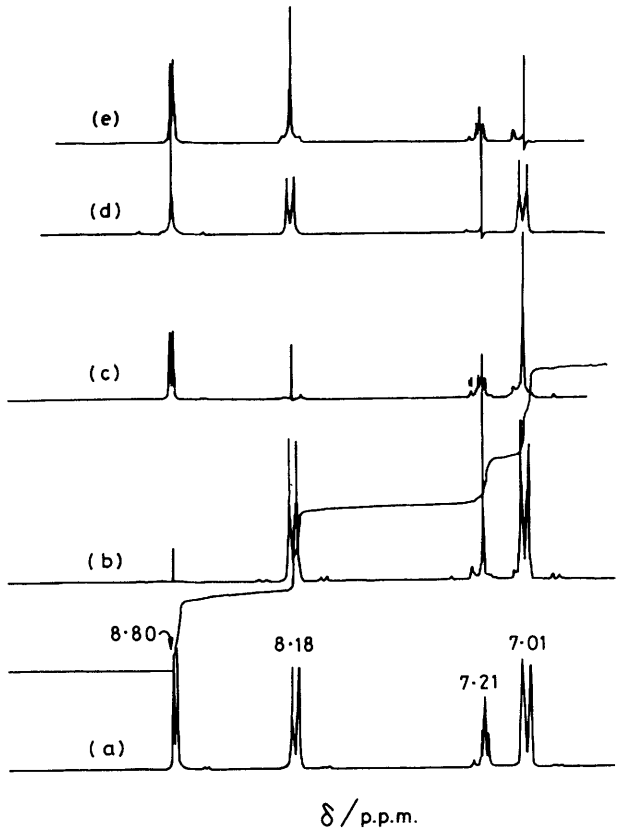


Figure 1. ^1H N.m.r. spectrum (250 MHz) of compound (6b). (a) Normal, (b) with irradiation at 2 200, (c) with irradiation at 2 045, (d) with irradiation at 1 802, (e) with irradiation at 1 752 Hz

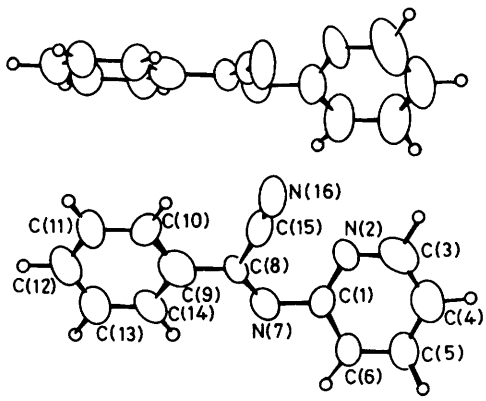


Figure 2. Perspective view of compound (5a) showing the crystallographic numbering scheme

readily identified by using the coupling and chemical shifts of pyridine.[5] The methyl group in the 7-position destroys the symmetry, so that the three individual carbons C(8), C(9), and C(10) can be observed at 139.62, 123.97, and 146.01 p.p.m. The quaternary carbons C(6) at 156.78 p.p.m. and C(5) at 138.30 p.m. are consistent with the deshielding of the carbon directly bonded to nitrogen and the effect of the C≡N group respectively. A ^{13}C n.m.r. spectral analysis of (6b) in $CDCl_3$ led to the required information regarding the structure of (6). Carbons C(8) and C(10) at 158.97 p.p.m. and C(9) at 118.86 p.p.m. respectively, were assigned by comparison with those for pyrimidine. The signal at 165.76 p.p.m. was assigned to C(6), and carbons C(1)—C(5) and C(11) were assigned by analogy with methoxybenzene and compounds (5a—e).

The correction of structures (3) and (4) to (5) and (6), and of the other derivatives described in the patent literature, was confirmed by *X*-ray analysis of the pyridyl compound (5a). Two perspective views of the molecule are shown in Figure 2. Pertinent bond lengths, and angles are summarized in Table 3 and the fractional co-ordinates of the atoms in Table 4. Anisotropic thermal parameters and structure factors are available as a Supplementary Publication (see Experimental section). Examination of the drawing of (5a) shows that the C≡N group is in the plane of the phenyl ring. Interestingly, the pyridine ring is twisted 38° from the plane of the phenyl ring system.

Ring-opening reactions of nitrogen bridgehead compounds have been described.[6] A possible intermediate in this cleavage is the nitrene (7), which could undergo rapid bond isomerism to yield the nitriles (5)—(6) (Scheme 2).

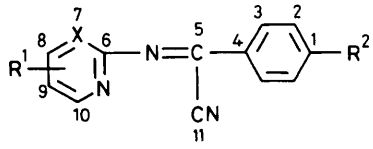
We found the imidazo[1,2-*a*]-pyridines and -pyrimidines to be particularly susceptible to ring-opening and then conversion into 3-amino derivatives by ring-closure rearrangement reactions. For example, heating compound (5c) at 120 °C with toluene–triethyl phosphite for 3 h caused the nitrogen of the pyridine to add across the nitrile to give 3-amino-7-methylimidazo[1,2-*a*]pyridine (8c) (Scheme 2) in 50% yield. The ^1H n.m.r. and mass spectra of this product are consistent with the

Table 1. Physical and spectral data for compounds (5), (6), (8), and (9)

Compd.	M.p. (°C)	Formula [a]	M^+	I.r.[b] (cm^{-1})	Chemical shift [c] (δ)
(5a)	79—81	$C_{13}H_9N_3$	207	2 215, 1 600, 880, 770	8.53 (m, 1 H), 8.12 (m, 2 H), 7.77 (dd, 1 H), 7.27 (m, 5 H)
(5b)	127—129	$C_{14}H_{11}N_3O$	237	2 220, 1 620, 870	8.57 (m, 1 H), 8.17 (d, 2 H), 7.77 (t, 1 H), 7.20 (m, 2 H), 7.07 (d, 2 H), 3.87 (s, 3 H)
(5c)	56—58	$C_{14}H_{11}N_3$	221	2 200, 1 600, 865	8.45 (d, 1 H), 8.21 (dd, 2 H), 7.54 (m, 3 H), 7.09 (m, 2 H), 2.42 (s, 3 H)
(5d)	100—102	$C_{15}H_{13}N_3O$	251	2 202, 1 600, 862	8.42 (dd, 1 H), 8.15 (d, 2 H), 6.48 (m, 4 H), 3.88 (s, 3 H), 2.40 (s, 3 H)
(5e)	111—113	$C_{14}H_{10}FN_3$	239	2 210, 1 600, 868	8.47 (m, 1 H), 8.25 (m, 2 H), 7.65 (d, 1 H), 7.27 (m, 3 H), 2.38 (s, 3 H) [d]
(6a)	97—99	$C_{12}H_8N_4$	208	2 220, 1 620, 1 410, 860	8.88 (d, 2 H), 8.30 (dd, 2 H), 7.60 (m, 3 H), 7.29 (t, 1 H)
(6b)	129—131	$C_{13}H_{10}N_4O$	238	2 220, 1 622, 1 404, 865	8.80 (d, 2 H), 8.18 (d, 2 H), 7.21 (t, 1 H), 7.01 (d, 2 H), 3.88 (s, 3 H)
(6c)	98—100	$C_{14}H_{12}N_4O$	252	2 220, 1 620, 880	8.64 (d, 1 H), 8.18 (d, 2 H), 7.02 (m, 3 H), 3.88 (s, 3 H), 2.58 (s, 3 H)
(8a) [d,e]	211—213	$C_{13}H_{11}N_3$	209	3 400, 1 630, 750	8.46 (m, 1 H), 8.10 (m, 2 H), 7.46 (m, 5 H), 7.15 (t, 1 H), 3.80 (NH_2)
(8b)	150—152	$C_{14}H_{13}N_3O$	239	3 420, 3 345, 1 630, 860	7.87 (m, 3 H), 7.43 (m, 1 H), 6.77 (4 H), 3.80 (s, OMe), 3.31 (NH_2)
(8c)	204—206	$C_{14}H_{13}N_3$	223	3 440, 3 280, 1 660, 680	7.92 (m, 3 H), 7.33 (m, 4 H), 6.60 (dd, 1 H), 2.36 (s, 7-Me), 3.30 (NH_2)
(8d)	194—196	$C_{15}H_{15}N_3O$	253	3 440, 3 240, 1 640, 1 250	7.92 (d, 1 H), 7.93 (d, 2 H), 7.26 (br, 1 H), 6.98 (d, 2 H), 6.58 (dd, 1 H), 3.83 (s, OMe), 2.36 (s, 7-Me), 3.20 (NH_2)
(8e) [d]	250—252	$C_{14}H_{12}FN_3$	241	3 440, 3 240, 1 630	8.53 (m, 1 H), 8.01 (m, 2 H), 7.33 (4 H), 2.55 (s, 8-Me), 2.48 (NH_2)
(9a)	220—222	$C_{12}H_{10}N_4$	210	3 340, 3 280, 1 610, 680	8.40 (m, 2 H), 8.01 (m, 2 H), 7.30 (m, 3 H), 6.80 (m, 1 H), 4.30 (NH_2)
(9b)	214—216	$C_{13}H_{12}N_4O$	240	3 400, 1 640, 1 260	8.32 (m, 2 H), 8.01 (d, 2 H), 7.02 (m, 3 H), 3.83 (s, OMe), 2.81 (NH_2)
(9c)	220—222	$C_{14}H_{14}N_4O$	254	3 300, 3 190, 1 620, 1 250	8.12 (m, 3 H), 6.88 (m, 3 H), 3.87 (s, OMe), 2.60 (s, 7-Me), 2.95 (NH_2)

[a] Satisfactory analytical data (±0.4% for C, H, and N) were reported for all new compounds listed in the Table. [b] In a KBr disk. [c] In $CDCl_3$. [d] In $(CD_3)_2SO$. [e] See ref. 3.

Table 2. ^{13}C Chemical shifts and assignments for compounds (5a—e) and (6a—c) [a]



Compd.	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	R^1	R^2
(5a)	133.46	129.17	128.90	133.92	141.31	159.42	118.54	138.39	123.06	149.11	111.65		
(5b)	[164.17]	114.62	130.95	126.89	140.53	159.79	118.24	138.30	122.60	149.02	111.79		55.66
(5c)	133.32	129.10	128.70	133.78	141.06	159.39	118.95	[149.84]	124.09	148.67	111.41	21.11	
(5d)	[163.85]	115.03	130.40	126.07	139.62	159.28	118.18	[149.89]	123.88	148.38	111.60	20.39	55.80
(5e) [b]	[171.65]	117.31	131.31	130.27	138.30	156.78	[128.12]	139.62	123.97	146.01	111.69	16.70	
	[159.06]	116.21	130.81	130.13									
(6a)	134.28	129.31	129.31	134.05	144.46	165.63		159.01	119.18	159.01	110.87		
(6b)	[164.81]	114.75	131.54	126.07	143.45	165.76		158.97	118.86	158.97	111.10		55.71
(6c)	[164.76]	114.75	131.54	126.25	143.45	165.74		[169.69]	118.40	158.46	111.15	24.09	55.71

[a] Values are in p.p.m. relative to Me_4Si; $CDCl_3$ solvent. [b] $(CD_3)_2SO$ solvent. Square brackets indicate substituted carbons.

structure (8), which is confirmed by comparison with the product (8c) from the reaction of (1a) with Sn–HBr (Table 1).

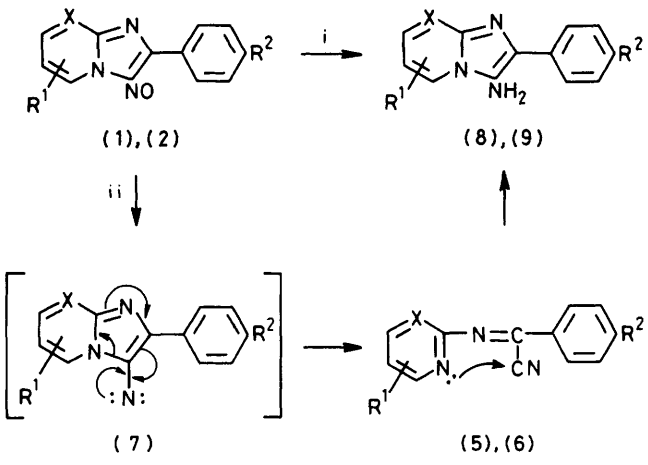
Experimental

M.p.s were determined on a Büchi capillary melting point apparatus and are not corrected. Elemental analyses were performed by the Microanalytical Center, ENSCM, Montpellier, and CNRS, Vernaison. Spectral measurements were taken using the following instruments: ^1H n.m.r. spectra were recorded on a Brucker WH 250 or a Brucker WH-180 spectrometer at 90 MHz; ^{13}C n.m.r. spectra were obtained at *ca.* 26 °C with proton-noise decoupling at 20.1 MHz with a Brucker WH-180 instrument. Chemical shifts are expressed relative to internal tetramethylsilane in $CDCl_3$ [or $(CD_3)_2SO$] at a concentration of *ca.* 5%. I.r. spectra were obtained on a Beckmann acculab spectrometer. Mass spectra were recorded on a LKB 2091 spectrometer at 70 eV [θ(source) = 180°].

Table 3. Bond distances (Å), angles (°), and torsion angles (°) of compound (5a) * with e.s.d.s in parentheses

1	2	3	4	1–2	1–2–3	1–2–3–4
N(2)	C(1)	C(6)		1.296(8)	123.3(6)	
N(2)	C(1)	N(7)	C(8)		118.7(5)	37.60
C(6)	C(1)	N(7)			117.7(6)	
C(1)	N(2)	C(3)			116.4(6)	
N(2)	C(3)	C(4)		1.34(1)	124.0(8)	
C(3)	C(4)	C(5)		1.37(1)	118.6(8)	
C(4)	C(5)	C(6)		1.35(1)	117.5(7)	
C(1)	C(6)	C(5)		1.359(9)	120.0(7)	
C(1)	N(7)	C(8)	C(9)	1.410(8)	121.7(5)	176.61
C(1)	N(7)	C(8)	C(15)			−5.70
N(7)	C(8)	C(9)	C(14)	1.273(7)	122.3(5)	180.08
N(7)	C(8)	C(15)	N(16)		122.0(5)	210.42
C(5)	C(6)			1.380(1)		
C(9)	C(8)	C(15)		1.487(8)	114.8(5)	
C(8)	C(9)	C(10)			118.5(6)	
C(3)	C(9)	C(14)			121.0(6)	
C(10)	C(9)	C(14)			120.5(6)	
C(9)	C(10)	C(11)		1.408(9)	118.5(6)	
C(10)	C(11)	C(12)		1.390(9)	120.6(6)	
C(11)	C(12)	C(13)		1.38(1)	120.5(6)	
C(12)	C(13)	C(14)		1.35(1)	121.5(6)	
C(9)	C(14)	C(13)		1.400(9)	118.4(6)	
C(8)	C(15)	N(16)		1.454(8)	172.8(6)	
C(13)	C(14)			1.392(9)		
C(15)	C(16)			1.143(8)		

* *X*-Ray numbering.



Scheme 2. *Reagents:* i, Sn/HBr; ii, $P(OEt)_3$

Compounds were purified by high-performance liquid chromatography (h.p.l.c.), Jobin-Yvon, on a preparative alumina column).

3-*Nitroso*-2-*phenylimidazo*[1,2-a]*pyridine* (1a).—This compound was prepared by the general method given in ref. 11.

2-(4-*Methoxyphenyl*)-3-*nitrosoimidazo*[1,2-a]*pyridine* (1b).—This compound was prepared according to the procedure of Almirante.[11]

7-*Methyl*-3-*nitroso*-2-*phenylimidazo*[1,2-a]*pyridine* (1c).—This compound was prepared by the general method: [11] m.p. 194—196 °C; δ ($CDCl_3$) 2.50 (s 3 H), 7.03 (m, 1 H), 7.57 (m, 4 H), 8.66 (m, 2 H), and 9.8 (d, 1 H).

2-(4-*Methoxyphenyl*)-7-*methyl*-3-*nitrosoimidazo*[1,2-a]*pyridine* (1d).—Compound (1d) was prepared by the general method: [11] m.p. 207—209 °C; δ ($CDCl_3$) 2.5 (s, 3 H), 3.91 (s, 3 H), 7.05 (m, 3 H), 7.53 (s, 1 H), 8.67 (d, 2 H), and 9.83 (d, 1 H).

2-(4-*Fluorophenyl*)-8-*methyl*-3-*nitrosoimidazo*[1,2-a]*pyridine* (1e).—This compound was prepared by the general method: [11] m.p. 229—231 °C; δ ($CDCl_3$) 2.73 (s, 3 H), 7.23 (m, 3 H), 7.63 (dd, 1 H), 8.71 (m, 2 H), and 9.82 (dd, 1 H).

3-*Nitroso*-2-*phenylimidazo*[1,2-a]*pyrimidine* (2a).—This compound was prepared according to the method of Pentimalli.[12]

2-(4-*Methoxyphenyl*)-3-*nitrosoimidazo*[1,2-a]*pyrimidine* (2b).—Compound (2b) was prepared according to the method of Hurst.[12]

2-(4-*Methoxyphenyl*)-7-*methyl*-3-*nitrosoimidazo*[1,2-a]*pyrimidine* (2c).—This compound was prepared by the general method: [11] m.p. 253—255 °C.

General Procedure for Compounds (5a—e) *and* (6a—c).—To triethyl phosphite (30 ml, 0.15 mmol) under nitrogen was added analytical grade 3-nitroso-2-phenylimidazo[1,2-*a*]-pyridine (2a—e) or -pyrimidine (3a—c) (0.04 mol). The mixture was refluxed for 5 min with stirring. During this time, the colour of the solution changed from green to brown. After being cooled, the excess of triethyl phosphite was removed under reduced pressure. The residue was chromatographed (neutral alumina, CH_2Cl_2 as eluant) to give a small amount of an unidentified red solid (0.1—0.2 g). Further elution yielded compounds (5a—e) or (6a—c) (51—80%) as pale yellow plates.

3-*Amino*-2-*phenylimidazo*[1,2-a]*pyridines* (8a—e).—*Method A*. A solution of (5a) (0.41 g, 0.002 mol) and triethyl phosphite

Table 4. Fractional co-ordinates for compound (5a) (× 10^4 for non-hydrogen atoms and × 10^3 for hydrogens) with e.s.d.s in parentheses

Atom	x/a (σ)	y/b (σ)	z/c (σ)	B_{eq}/B_i
C(1)	3 282(2)	2 133(5)	6 086(10)	4.6
N(2)	3 013(2)	1 197(4)	5 795(9)	4.9
C(3)	2 467(3)	1 285(6)	5 714(15)	8.9
C(4)	2 186(3)	2 285(7)	5 942(13)	7.0
C(5)	2 474(3)	3 254(6)	6 187(14)	6.8
C(6)	3 037(3)	3 171(5)	6 224(12)	5.9
N(7)	3 860(2)	2 095(4)	6 114(7)	4.4
C(8)	4 119(2)	1 256(4)	6 780(8)	2.9
C(9)	4 727(3)	1 174(6)	6 729(9)	6.1
C(10)	5 024(2)	2 047(5)	5 877(9)	5.0
C(11)	5 592(3)	1 961(6)	5 806(10)	5.9
C(12)	5 858(3)	1 032(6)	6 528(10)	5.5
C(13)	5 570(3)	196(6)	7 344(10)	5.5
C(14)	5 000(3)	239(5)	7 471(9)	4.5
C(15)	3 846(2)	324(5)	7 697(9)	4.6
N(16)	3 680(2)	−417(5)	8 524(9)	5.6
H(30)	227(2)	59(5)	536(9)	8.8
H(40)	177(2)	229(6)	592(9)	9.3
H(50)	229(3)	401(6)	641(10)	11.0
H(60)	329(2)	385(5)	645(8)	8.4
H(100)	482(2)	274(5)	535(8)	7.7
H(110)	580(2)	257(6)	515(9)	8.8
H(120)	627(2)	99(5)	650(9)	8.5
H(130)	575(2)	−48(4)	794(8)	6.5
H(140)	479(2)	−40(5)	810(8)	8.7

(5 ml) was refluxed for 3 h with stirring under a flow of dry nitrogen gas. After being cooled, the triethyl phosphite was removed under reduced pressure and the residue chromatographed (neutral alumina, CH_2Cl_2) to give 3-amino-2-phenylimidazo[1,2-*a*]pyridine (8a) (0.12 g, 29%), m.p. 111—113 °C.

Method B. To a suspension of tin (1 g) in ice-cold, concentrated HBr (30 ml) was added, during 0.5 h, 3-nitroso-2-phenylimidazo[1,2-*a*]-pyridine (or -pyrimidine) (1a—e) or (2a—c) (1 g) with stirring. After being stirred for 3 h, the precipitate was filtered, taken up in H_2O (30 ml), and the suspension made alkaline with NH_4OH. The solid was extracted overnight with CH_2Cl_2 in a Soxhlet apparatus. The CH_2Cl_2 was dried (Na_2SO_4) and filtered and the solvent evaporated, producing compounds (8a—e) and (9a—c) (Table 1) which were recrystallized from $CHCl_3$ to give yellow crystals identical with the products prepared by method A. These compounds were also prepared by the general method.[10]

X-*Ray Analysis.*—*N*-(2-Pyridyl)benzimidoyl cyanide (5a) crystallized in the orthorhombic system with a = 24.377 (6), b = 11.729(3), and c = 7.534(2) Å; space group *Pbca* with a calculated density of 1.27 g/cm^3 (Z = 8). The intensity data were collected on a fully automated Nonius CAD-4 diffractometer using graphite monochromated Cu-K_α radiation (1.54178 Å) and a ωθ scan (ω/θ = 1). Of the 1 831 unique reflections with θ <65° measured in this fashion, 716 were considered as observed after correction for Lorentz-polarization effects. The structure was solved by direct methods [7] and electron density synthesis. The nitrogen positions were determined in two steps: (i) the existence of a CN function became obvious as soon as we considered the interatomic distances and the valency angles before refinement [C(15)–N(16) = *ca.* 1.15 Å, C(8)–C(15)–N(16) = *ca.* 170°], and (ii) block diagonal matrix least-squares refinements of non-hydrogen atoms (all considered as carbons) affected by anisotropic temperature factors were followed by difference Fourier maps from which the hydrogens were located; consequently, the absence of H linked to C-2 and -7, the short bond C(7)–C(8), and the good agreement with the n.m.r. data allowed us to locate the two remaining nitrogens at positions 2 and 7 and to propose the chemical structure of the compound. Further refinements after introduction of H atoms affected by isotropic temperature factors led to the current minimum residual of 0.061. Structure factor tables and anisotropic temperature factors for compound (5a) are available as a Supplementary Publication * (SUP No. 23713, 13 pages).

Individual bond distances and angles agree well with accepted values. Crystalline cohesion is ensured by strong van-der-Waals contacts.

* For details of the Supplementary Publications Scheme see Instructions for Authors (1983) in *J. Chem. Soc., Perkin Trans. 1*, 1983, Issue 1.

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