Carbon-Nitrogen Bond Formation in Cyclisations by Deoxygenation, Thermolysis, or Photolysis of Phenylimidazo[1,2-*a*]pyridine Systems: Access to Pyrido[1′,2′:1,2]imidazo[4,5-*b*]indoles

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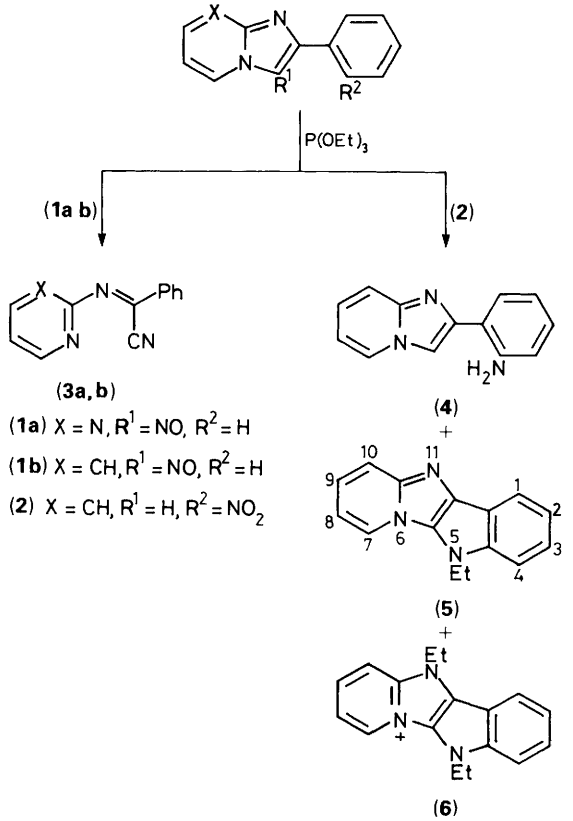
Reductive cyclisation of 2-(2-nitrophenyl)imidazo[1,2-*a*]pyridine with triethyl phosphite gives the indolic structures (**5**) and (**6**). The latter are of interest because of preferential C insertion rather than reaction of the nitrene at N-1 of the imidazole ring. 2D N.m.r. confirms structure (**5**). Both thermolysis or photolysis of the representative 2-(2-azidophenyl)imidazo[1,2-*a*]pyridines (**7**) and (**8**) are also reported and shown to produce novel indole, cinnoline, and benzofuran structures in an extremely facile fashion.

The azaindolizines containing indolic structures are currently attracting increased interest for both synthetic and biological reasons.[1] Deoxygenation of *C*-nitroso or nitro derivatives by $P(OEt)_3$ is known to give reductive cyclisation to a variety of heterocyclic systems *via* a nitrene when an excess of reducing agent is used.[2] Recently, it has been reported that the reaction of 3-nitrosoimidazo[1,2-*a*]pyridine (or pyrimidine) with triethyl phosphite does not lead to products described in the literature as pyrido-(or pyrimido-)[1′,2′:1,2]imidazo[4,5-*b*]indoles,[3] but the open-chain derivatives, *N*-(2-pyridyl)- and *N*-(2-pyrimidyl)-benzimidoyl cyanides.[4]

In continuation of our studies on the reactivity of nitrogen bridgehead azaindolizines, we have now investigated the possibility that a thermal reaction involving $P(OEt)_3$ and 2-*o*-nitrophenylimidazo[1,2-*a*]pyridine gives the indolic systems by heterocyclisation. We report here the synthesis of pyrido-[1′,2′:1,2]imidazo[4,5-*b*]indoles (**5**) and (**6**) as potential antihypertensive compounds. Thermolysis and photolysis of the azido derivatives from 2-phenylimidazo[1,2-*a*]pyridine structure is also reported.



Results and Discussion

Attempted conversion of the nitro derivative (**2**) (prepared by condensation of ω-bromo-*o*-nitroacetophenone with 2-aminopyridine) into an indole structure by treatment with an excess of freshly distilled $P(OEt)_3$ under reflux and a flow of dry nitrogen gas gave compounds (**4**)—(**6**); no ring expansion to give an azepine was observed.[5] Reduction of the starting nitro compound (**2**) to the corresponding amine (**4**) (2%) is indicative of singlet nitrene participation.[6] In principle, the singlet nitrene has two sites for attack, at C-3 or N-1 of the imidazole ring. Generally the nitrene prefers to attack electron-rich nitrogen (pyridine) rather than initiate C insertion at the *ortho* position;[5] exceptions to this are nitrenes generated from 5-(2-nitrophenyl)-2-phenylthiazole,[7] azidocarbostyryls[8] and nitrophenylpyridine.[9] Examination of the mass spectral fragmentation patterns of (**5**) gives its molecular weight (M^+) as 235, with a ready loss of C_2H_5 ($M^+ - 29$). The ethyl group probably derives from alkylation of the intermediate indole.

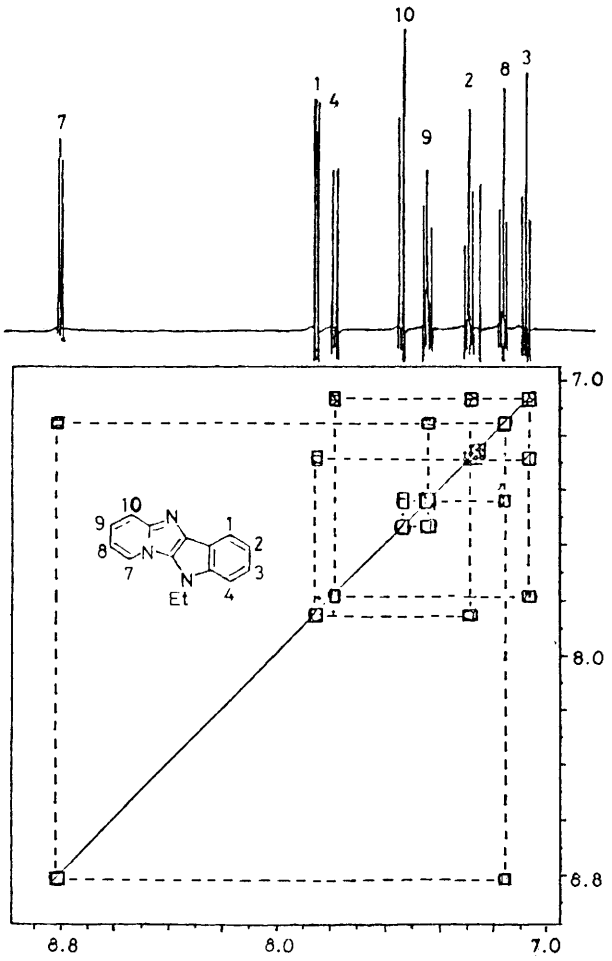
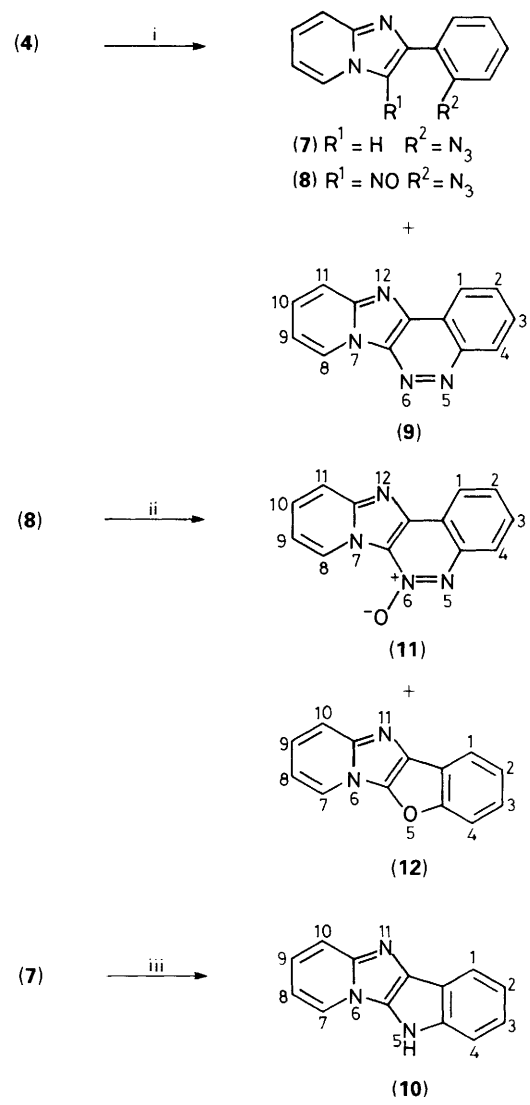


Figure 1. Contour map of the ^1H–^1H shift correlated spectrum (500 MHz; $CDCl_3$) in the aromatic region δ 7—8.8

The ^1H n.m.r. spectrum and 2D homonuclear correlated spectrum (COSY) of the tetracycle (**5**) are shown in Figure 1. Proton assignment was made on the basis of 2D COSY experiments and proton coupling constants. In addition to the ethyl signals at δ 1.71 and 4.62, the COSY procedure gives unequivocally the following values: H(1)(7.86)–H(2)(7.30)–H(3)(7.08)–H(4)(7.79) and H(7)(8.82)–H(8)(7.17)–H(9)(7.46)–H(10)(7.54). The position and the distinction between pyridine and phenyl resonances was made by comparison with similar assignments for imidazopyridine[10] and carbazole.[11] Thus $J_{7,8}$ and $J_{9,10}$ are normally in the range 6.2—6.8 and 9—9.5 Hz, respectively. In addition, the magnitude of $J_{1,2}$ coupling is known to be generally lower than $J_{3,4}$ coupling and in the range of 8—8.3 Hz for indole and carbazole.[11] Compound (**6**) yields ions at *m/z* 264, 235, and 206 by loss of two ethyl groups. No ^{31}P signal was detected from phosphoric acid in the region accepted for phosphonate.[12] The COSY spectrum gives H(1)(7.60)–H(2)(7.55)–H(3)(7.39)–H(4)(7.92) and H(7)-(9.75)–H(8)(7.65)–H(9)(7.88)–H(10)(8.53) connectivities. The strong deshielding revealed by the signals from 7-H to 10-H suggest that a positive charge is developed on N-6. This is consistent with the quaternisation data reported for imidazo-[1,2-*a*]pyridines.[13] The ^{13}C n.m.r. spectrum for (**6**)[14] is in accord with the proposed structure: eight aromatic CH, five quaternary carbons, and four alkyl carbons (CH_2 resonate at δ 40 and 42 p.p.m.) provide further confirmation.

In order to avoid the *N*-alkylation of the indolic structure, we have now investigated the photolysis and the thermolysis of the azido derivatives from (**4**).



Hydrogenation of the nitro group gave the amine (**4**) (92%) and this on treatment with $NaNO_2/HCl/NaN_3$ at 0—2 °C for 1 h gave compounds (**7**), (**8**), and pyrido[1′,2′:1,2]imidazo-[5,4-*c*]cinnoline (**9**) (82%). The structure of the product (**8**) was established on the basis of its ^1H n.m.r. spectrum which revealed eight signals, with deshielding of the 5-H signal suggesting a *peri* effect.[15] This structural assignment was supported by mass spectral evidence [*m/z* 264 (M^+, 0.2) and 236 (M − 28, 50)] and by an elemental analysis. Confirmation of this structural assignment was made by an independent synthesis of compound (**8**) from (**7**) with sodium nitrite in acetic acid. The ^1H n.m.r. spectrum of the cinnoline (**9**) revealed two characteristic ABXY systems[16] and the absence of the imidazole signal. The mass spectrum showed loss of nitrogen from the molecular ion behaviour reported earlier for benzo[*c*]cinnoline.[17] Thus, the ion at *m/z* 220 gave rise to the pyridoimidazophenylene radical ion (*m/z* 192). Finally, reaction of sodium azide on the diazotized compound formed from (**4**) in sodium acetate buffer solution at 0 °C produced the azides (**7**) (13.6%) and (**8**) (5.3%). The abundant ions $[M - N_2]^{+\cdot}$ [*m/z* 207 for (**7**) and 236 for (**8**)] and the remainder of the fragmentation patterns were in accord with loss of N_2[18] to give the tetracyclic structures (**10**) and (**11**) respectively.

Photolysis of the azide (**7**) in methylene dichloride in order to

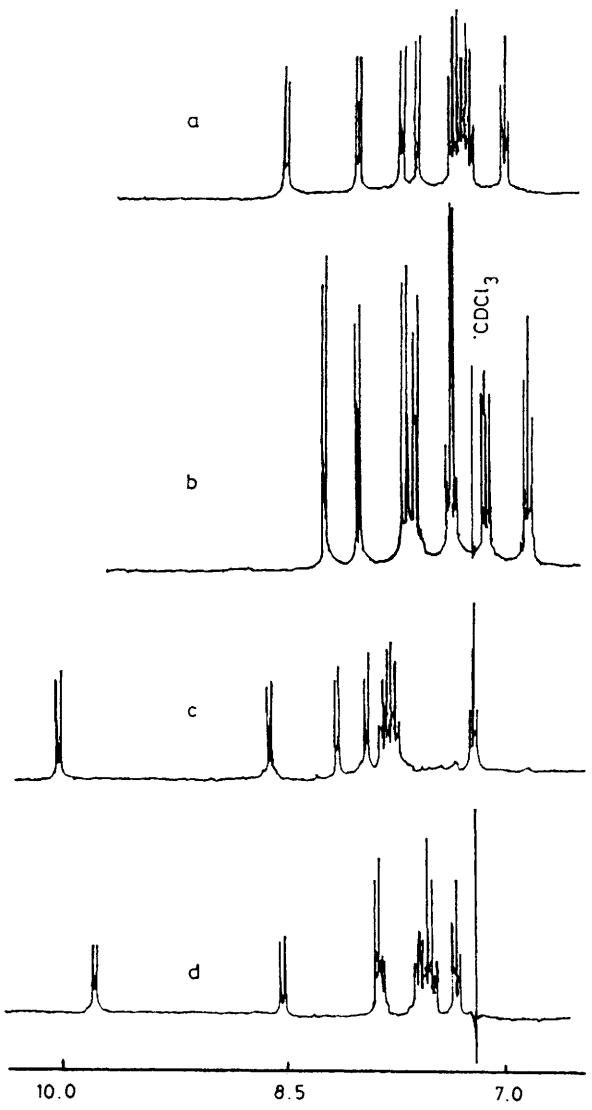


Figure 2. ^{1}H N.m.r. spectra (300 MHz) of (a) (**10**) (CD_3OD); (b) (**12**) ($CDCl_3$); (c) (**11**) ($CDCl_3$); and (d) (**6**) ($CDCl_3$)

optimise singlet pathways[19] gave compound (**10**), the mass spectrum of which showed *m/z* 207 (M^+, 100) and 206 (M − H, 30). The ^{1}H n.m.r. spectrum in CD_3OD showed eight aromatic signals (four doublets at δ 8.45, 7.98, 7.70, and 7.61, three triplets centred at δ 7.33, and a triplet at δ 7.05): these signals, consistent with structure (**10**), were assigned using the COSY procedure. The azide (**7**) was thermolysed at 185 °C as a dilute solution in anhydrous 1,2,4-trichlorobenzene. Two fractions were obtained and identified as the azide (**7**) and a set of two products which could not be purified. Attempted thermolysis of (**7**) proved unsatisfactory at 100—180 °C and led mainly to tar formation >185 °C.

Decomposition of the azide (**8**) in hot trichlorobenzene gave two products: the cinnoline *N*-oxide (**11**) (52%) and the benzofuran (**12**) (14%). The cinnoline *N*-oxide (**11**) showed in its ^{1}H n.m.r. spectrum a strong *peri* effect for 8-H.[20] The COSY procedure gives unequivocally the H(1)(8.17)–H(2)(7.83)–H(3)(7.83)–H(4)(8.6) and H(8)(9.95)–H(9)(7.27)–H(10)(7.83)–H(11)(7.98) connectivities. This structure was confirmed on the basis of mass spectral evidence which showed ions at *m/z* 236 (M^+, 100), 220 (M − O), and 206 (M − NO): the last two ions are typical of this heterocyclic entity.[21] Mass spectral fragmentation of the benzofuran (**12**) occurs *via* the ions 208 (M^+), 180 (M − CO), and 179 (M − CO − H) in accord with similar results for dibenzofuran.[22] No compounds containing an N–N bond were detected.

Experimental

General Details.—M.p.s were taken on a Büchi capillary apparatus and are not corrected. ^{1}H N.m.r. spectra were recorded with Bruker WM 500 (500 MHz FT), WM 300 (300 MHz FT), WM 360 (360 MHz FT) or Varian 360 (60 MHz) spectrometers. ^{13}C N.m.r. spectra were performed on a Bruker MSL 300 instrument operating at 75 MHz. The ^{13}C chemical shifts are reported in p.p.m. from TMS with the centre resonance of $CDCl_3$ as an internal reference for ^{13}C (77.0 p.p.m.) and with the small amount of residual $CHCl_3$ as an internal reference for the ^{1}H spectrum (7.24 p.p.m.). All COSY spectra (**5**), (**6**), (**10**), (**11**), and (**12**) were obtained by using Jeener's two-pulse sequence 90° t_1-Pw-acquire. The mass spectra were recorded with a JEOL JMS DX 300 instrument or a LKB 2091 spectrometer. Compounds were purified by high-performance liquid chromatography (h.p.l.c.), Jobin-Yvon, on a preparative alumina column using Merck alumina (70—230 mesh). The photolysis solution was irradiated internally using a 100 W medium-pressure mercury lamp (Hanovia) with a Pyrex filter.

2-(2-*Nitrophenyl*)*imidazo*[1,2-a]*pyridine* (**2**).—To a solution of freshly distilled 2-aminopyridine (9.4 g, 0.1 mol) in ethanol (200 ml), was added *o*-nitro-ω-bromoacetophenone (24.4 g). The mixture was stirred and heated at 70 °C for 4 h after which the solvent was removed under reduced pressure and the residue taken up in water (200 ml), made alkaline with Na_2CO_3, and extracted with methylene dichloride. The extract was evaporated and the residue was chromatographed (neutral alumina CH_2Cl_2 as eluant) to give (**2**) (72%), m.p. 151—153 °C (Found: C, 65.45; H, 3.65; N, 17.65. $C_{13}H_9N_3O_2$ requires C, 65.27; H, 3.77; N, 17.57%); *m/z* 239 (M^+); δ(360 MHz; $CDCl_3$) 8.12 (d, 1 H), 8.02 (d, 1 H), 7.8 (s, 1 H), 7.74 (d, 1 H), 7.65 (m, 2 H), 7.44 (dd, 1 H), 7.21 (dd, 1 H), and 6.81 (dd, 1 H).

N-*Ethylpyrido*[1′,2′-1,2]*imidazo*[4,5-b]*indole* (**5**).—To freshly distilled triethyl phosphite (30 ml, 0.15 mol) under nitrogen was added 2-(2-nitrophenyl)imidazo[1,2-*a*]pyridine (**2**) (0.04 mol). The stirred mixture was refluxed for 4 h after which it was cooled and the excess of triethyl phosphite removed under reduced pressure. Chromatography (alumina, CH_2Cl_2) gave the crude product (**5**) which crystallised from CH_2Cl_2 to give (**5**) (1.96 g, 23.6%) as yellow prisms, m.p. 260—262 °C (Found: C, 76.3; H, 5.4; N, 18.05. $C_{15}H_{13}N_{13}$ requires C, 76.59; H, 5.53; N, 17.87%); *m/z* (relative intensity) (M^+, 60), 206 (M − C_2H_5, 91), 169 (60), and 78 (100); δ_H(500 MHz; $CDCl_3$), 8.82 (d, *J* 6.6 Hz, 7-H), 7.86 (d, *J* 8.1 Hz, 1-H), 7.79 (d, *J* 8.3, 4-H), 7.54 (d, *J* 9.1, 10-H), 7.46 (dd, 9-H), 7.30 (dd, 2-H), 7.17 (dd, 8-H), 7.08 (dd, *J* 7.4, 3-H), 4.62 (q, 2 H), and 1.71 (t, 3 H); δ_C(125 MHz; $CDCl_3$) δ(CH) 14.82, 41.42, 109.02, 113.77, 117.02, 118.35, 122.49, 124.90, 126.32, and 133.52. Further elution gave the amine (**4**) which was identical in all respects with a sample prepared by the following procedure. Elution with methylene dichloride–methanol (96:4, v/v) gave (**6**) (3.17 g, 30%), m.p. 310—312 °C; *m/z* 264 (M^+, 7) 235 (M − C_2H_5, 66), 206 (M − C_2H_5 − C_2H_5, 100), and 78 (85); δ_H(300 MHz; $CDCl_3$) 9.75 (d, *J* 6.9, 7-H), 8.53 (d, *J* 9.2, 10-H), 7.92 (d, *J* 8.3, 4-H), 7.88 (dd, 9-H), 7.65 (dd, 8-H), 7.60 (d, *J* 8.1, 1-H), 7.55 (dd, 2-H), 7.39 (dd, 3-H), 5.01 (q, 4 H), 1.73 (t, 3 H), and 1.55 (t, 3 H); δ_C(75.47 MHz; $CDCl_3$) 140.32, 138.91, 131.66 (CH), 127.72, 127.12 (CH), 126.46 (CH), 121.98 (CH), 119.03 (CH), 118.35, 117.50 (CH), 112.16, 111.91 (CH), 111.41 (CH), 42.87 (CH_2), 40.46 (CH_2), 16.26 (CH_3), and 15.18 (CH_3).

2-(2-*Aminophenyl*)*imidazo*[1,2-a]*pyridine* (**4**).—To a stirred suspension of tin (1.6 g) in ice-cold, concentrated HBr (3 ml) was added, during 0.4 h, 2-(2-nitrophenyl)imidazo[1,2-*a*]pyridine (**2**) (1.4 g). After the mixture had been stirred for 4 h the precipitate was filtered off, taken up in water (3 ml), and the suspension made alkaline with NH_4OH. After evaporation under reduced pressure, the residue was chromatographed (neutral alumina, CH_2Cl_2 as eluant) to give (**4**) as pale white plates (1.2 g, 92% yield), m.p. 136—138 °C (Found: C, 74.55; H, 5.4; N, 20.0. $C_{13}H_{11}N_3$ requires C, 74.64; H, 5.26; N, 20.1%); δ(60 MHz; $CDCl_3$) 8.01 (d, 1 H), 7.73 (s, 1 H), 7.53 (m, 2 H), 7.10 (m, 2 H), 6.60 (m, 3 H), and 5.51 (s, 2 H, NH_2).

2-(2-*Azidophenyl*)*imidazo*[1,2-a]*pyridine* (**7**).—*Method A.* A solution of (**4**) (0.836 g, 0.004 mol) in water (24 ml) containing 12M HCl (1 ml) was cooled to 0 °C and treated portionwise with a solution of sodium nitrite (0.32 g) in water (1 ml). After the mixture had been stirred for 10 min at 2 °C, a solution of sodium azide (0.3 g) in water (1 ml) was added. The mixture was stirred at 0—2 °C for 1 h, made basic with concentrated aqueous sodium hydroxide, and extracted with methylene dichloride. The organic extract was dried (Na_2SO_4) and evaporated and the residue was chromatographed on silica gel (foil wrapped to exclude light). Elution with Et_2O yielded the azide (**7**) (1%), m.p. 100—102 °C (Found: C, 66.5; H, 3.7; N, 29.8. $C_{13}H_9N_5$ requires C, 66.38; H, 3.83; N, 29.79%), *m/z* 235 (M^+, 9.4), 207 (80.1), 179 (26.3), and 78 (base peak); $\nu_{max.}$(KBr) 2 102, 1 631, 1 294, and 704 cm^{-1}; δ(60 MHz; $CDCl_3$) 8.56 (m, 1 H), 8.18 (s, 1 H), 8.00 (d, 1 H), 7.66 (d, 1 H), 7.25 (m, 3 H), 7.13 (dd, 1 H), and 6.61 (dd, 1 H). Further elution gave the nitroso compound (**8**) (trace), m.p. 170—172 °C (Found: C, 59.15; H, 3.1; N, 31.65. $C_{13}H_8N_6O$ requires C, 59.09; H, 3.03; N, 31.81%); $\nu_{max.}$(KBr) 2 100 (N_3) and 1 622 cm^{-1} (CN); *m/z* 264 (M^+, 0.2), 236 ($M - N_2$, 50), 206 ($M - N_2 - NO$, 47), and 78(100); δ(60 MHz; $CDCl_3$) 9.93 (d, 1 H), 8.01 (m, 3 H), and 7.50 (m, 4 H). Further elution from the column, using Et_2O–MeOH (96:4 v/v) gave a mixture separated by chromatography on neutral alumina. Elution with methylene dichloride gave pyrido[1′,2′:1,2]imidazo[5,4-*c*]-cinnoline (**9**) (0.72 g, 82%), m.p. 274—276 °C (Found: C, 71.05; H, 3.7; N, 25.25. $C_{13}H_8N_4$ requires C, 70.91; H, 3.64; N, 25.45%); *m/z* 220 (M^+, 100) and 192 ($M - 28$, 30); δ(60 MHz; $CDCl_3$) 9.40 (d, 1 H), 8.81 (m, 2 H), 7.95 (m, 4 H), and 7.25 (dd, 1 H).

Method B. A solution of (**4**) (0.90 g) in water (7.8 ml) and 12M HCl (2.4 ml) was cooled to 0 °C and treated portionwise with a solution of sodium nitrite (0.46 g) in water (1.6 ml). After being stirred for 10 min at 0 °C, the solution was added dropwise to vigorously stirred CH_3CO_2Na (3.1 g) and sodium azide (0.62 g) in water (24 ml) at 0 °C. Stirring was continued 2 h at 20 °C. The aqueous mixture was extracted with methylene dichloride and the organic extract was dried (Na_2SO_4) and evaporated. The residue was chromatographed as described above, with 13.6, 5.3, and 54.8% yield of the azide (**7**), the nitroso compound (**8**), and the cinnoline (**9**), respectively.

2-(2-*Azidophenyl*)-3-*nitrosoimidazo*[1,2-a]*pyridine* (**8**).—To a solution of 2-(2-azodiphenyl)imidazo[1,2-*a*]pyridine (9.2 g, 0.395 mmol) in acetic acid (2 ml) at 20 °C, was added in 1 h a solution of sodium nitrite (400 mg, 5.79 mmol) in water (3 ml). After cooling, the solution was made alkaline with Na_2CO_3 and extracted with methylene dichloride. The extract was dried and evaporated and the residue was chromatographed on neutral alumina with CH_2Cl_2 as eluant to yield the product (**8**) (5.6 g, 54%).

Thermal Decomposition of the Azide (**7**).—A solution of the azide (**7**) (0.1 g) in anhydrous 1,2,4-trichlorobenzene (2 ml) was added dropwise over 5 min to vigorously stirred 1,2,4-trichlorobenzene (10 ml) under dry nitrogen at 185 °C. The solution was further heated for 0.5 h after which time no azide could be detected (i.r.). The solvent was evaporated and the residue was chromatographed on silica gel, with CH_2Cl_2 as eluant to afford first trichlorobenzene (5.3 g); next 2-(2-azidophenyl)imidazo[1,2-*a*]pyridine (**7**) was eluted and this crystallised as white plates (0.012 g). Further elution gave a complex product mixture (0.066 g), the ^1H n.m.r. spectrum of which was too complex to analyse.

Thermolysis of the Azide (**8**).—A solution of the azide (**8**) (1 g) in 1,2,4-trichlorobenzene (5 ml) was heated at 185 °C with vigorous stirring, under nitrogen. Heating was continued for 30 min. After evaporation of the solvent, the residue was chromatographed on neutral alumina. Elution with CH_2Cl_2 yielded trichlorobenzene. Further elution gave (**12**) (0.45 g), m.p. 198—200 °C (Found: C, 74.9; H, 4.0; N, 13.6. $C_{13}H_8N_2O$ requires C, 75.0; H, 3.85; N, 13.46%); *m/z* 208 (M^+, 90), 180 ($M - CO$, 76), 179 ($M - CO - H$, 50), and 78 (100); δ(300 MHz; $CDCl_3$) 8.20 (d, 1 H, *J* 6.7 Hz, 7-H), 7.99 (m, 1 H, 1-H), 7.69 (d, 1 H, *J* 9 Hz, 10-H), 7.64 (m, 1 H, 4-H), 7.39 (m, 2 H, 2-H, 3-H), 7.18 (t, 1 H, 9-H), and 6.92 (t, 1 H, 8-H). Further elution with CH_2Cl_2 gave (**11**) (0.31 g), m.p. 296—298 °C (Found: C, 66.15; H, 3.5; N, 23.6. $C_{13}H_8N_4O$ requires C, 66.1; H, 3.39; N, 23.72%); *m/z* 236 (M^+, 100), 220 ($M - O$, 12), 206 ($M - NO$, 29), and 78 (76); δ(300 MHz; $CDCl_3$) 9.95 (d, 1 H, *J* 7 Hz, 8-H), 8.60 (d, 1 H, *J* 8 Hz, 4-H), 8.17 (d, 1 H, *J* 8 Hz, 1-H), 7.98 (d, 1 H, *J* 9.1, 11-H), 7.86 (d, 1 H, 2-H), 7.81 (m, 1 H, 3-H), 7.79 (m, 1 H, 10-H), and 7.27 (t, 1 H, 9-H).

Photolysis of the Azide. (**7**).—Using the apparatus described at the beginning of the Experimental section, with water cooling for an ambient temperature reaction, pure nitrogen was passed through the solution of (**7**) (0.4 g) in CH_2Cl_2 (200 ml). The reaction was monitored by following the disappearance of the azide i.r. absorption (**3h**). After removal of the solvent, the residue was chromatographed on neutral alumina. Elution with CH_2Cl_2–MeOH (90:10, v/v) gave (**10**) (0.22 g), m.p. 303—305 °C (Found: C, 75.4; H, 4.5; N, 20.05. $C_{13}H_9N_3$ requires C, 75.36; H, 4.35; N, 20.29%); *m/z* 207 (M^+, 100), 206 ($M - H$, 42), 179 (M – HCN), and 78 (35); δ(300 MHz, CD_3OD), 8.45 (d, *J* 6.6 Hz, 7-H), 7.98 (d, *J* 7.5 Hz, 1-H), 7.70 (d, *J*, 9 Hz, 10-H), 7.61 (d, *J* 8.2, 4-H), 7.38 (t, 3-H), 7.33 (t, 9-H), 7.28 (t, 2-H), and 7.05 (t, 8-H).

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