peri-Substituted Imidazo[1,2-*a*]pyridines. A New Reductive Elimination Reaction

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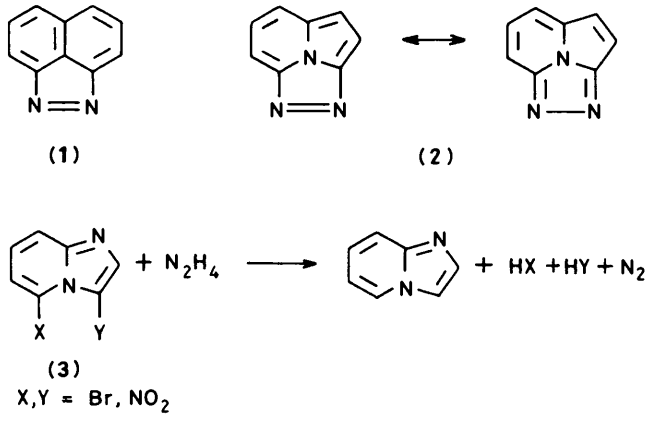
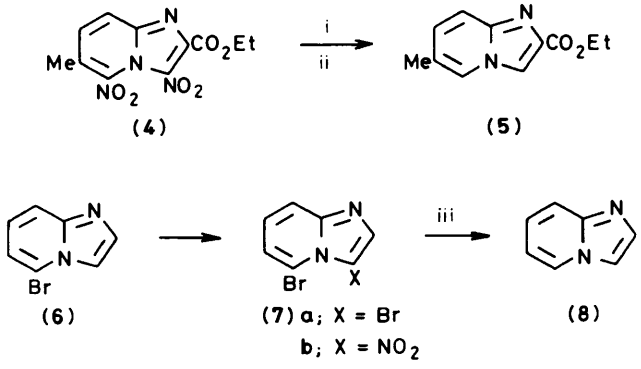
A new reductive elimination reaction of 3,5-disubstituted imidazo[1,2-*a*]pyridines (**3**) with hydrazine is reported. Thus on treatment of the 3,5-dibromo (**7a**), 5-bromo-3-nitro (**7b**), and 3,5-dinitro (**4**) derivatives with hydrazine hydrate in hot ethanol, the bromine and nitro groups are replaced by hydrogen. A mechanism based on the conjugated relationship of these *peri*-substituents is proposed and used to explain the reported conversion of 1,3,5-trichloro-2,4,6-trinitrobenzene (**9**) into 1,3-dichloro-4,6-dinitrobenzene (**10**). A variety of other 3-nitro-5-substituted imidazo[1,2-*a*]pyridines (**15**)—(**18**) is described, but these could not be cyclised to 1,2,4-triazacyclopentindenes. The 3-amino-5-methoxycarbonyl derivative (**19a**) cyclises to the triazacyclopentindenone (**20**) with sodium methoxide.

In view of the very high reactivity of benz[*c*,*d*]indazole (**1**),[1,2] stable only in dilute solution,[3] we tried, unsuccessfully, to synthesize a derivative of the unknown 1,2,7b-triazacyclopent-[*cd*]indene system (**2**) for comparison. Although (**2**) has a more strained σ-bond framework than (**1**) it should be stabilised by delocalisation of its conjugated 10 π electron periphery. In the course of preparing appropriately '*peri*' substituted imidazo-[1,2-*a*]pyridines (**3**) we have uncovered a new reductive elimination process, summarised in Scheme 1.



Scheme 1.

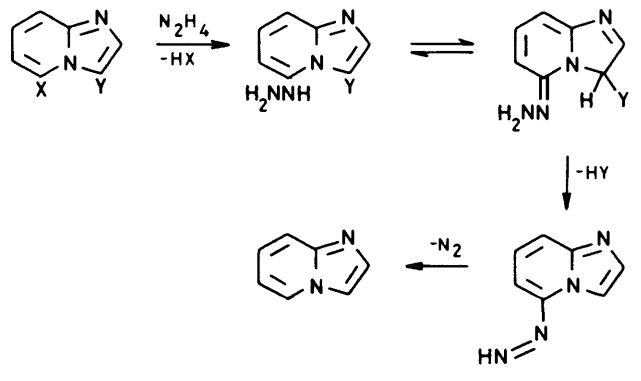
Our initial intention was to reduce the nitro groups of compound (**4**),[4] the only reported 3,5-dinitro derivative of the indolizine ring system, either partially with N–N bond formation, or completely to the diamine. Various attempts with alkaline glucose, alkaline sodium sulphide, zinc and hydrochloric or formic acid, and catalytic hydrogenation were all unsuccessful, giving multicomponent air-sensitive mixtures. However, reduction with hydrazine hydrate and palladised charcoal gave, unexpectedly and as the only stable product, the denitrated compound (**5**). In contrast, similar treatment of the mono-nitro derivative, ethyl 6-methyl-3-nitroimidazo[1,2-*a*]-pyridine-2-carboxylate, gave the expected 3-amino compound. This suggests that a different, non-reductive pathway was available to the dinitro compound (**4**), and so the hydrazine reaction was repeated without the palladium, and this resulted in a similar yield of the same denitrated product (**5**). Thus the leaving group ability, in nucleophilic aromatic substitution, of the nitro group may be the significant factor. To test this, the



Scheme 2. *Reagents:* i, N_2H_4·H_2O, EtOH; ii, Pd–C; iii, N_2H_4·H_2O

3,5-dibromo (**7a**) and 5-bromo-3-nitroimidazo[1,2-*a*]pyridine (**7b**), prepared from the 5-bromide (**6**) (Scheme 2), were treated with hydrazine hydrate in refluxing ethanol and in hot dimethylformamide (DMF). In each case imidazo[1,2-*a*]pyridine (**8**) was formed in moderate yield. Treatment of the bromo-nitro compound (**7b**) with hydrazine hydrate in DMF at room temperature gave a red product which, though detectable by t.l.c., could not be isolated cleanly owing to its rapid decomposition; it was probably the intermediate 5-hydrazino-3-nitroimidazo[1,2-*a*]pyridine.

A possible mechanism for the loss of both 3,5-substituents is shown in Scheme 3. This involves displacement of group X by hydrazine, proton tautomerism, extended elimination of HY,

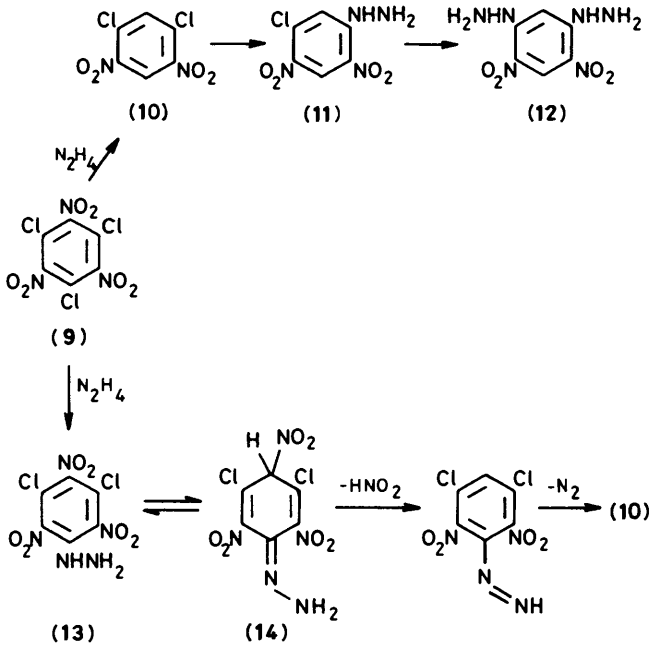


Scheme 3.

and loss of nitrogen from the di-imide. Nucleophilic substitution in the, activated, 5-position of indolizine[5] and imidazo[1,2-*a*]pyridine derivatives[6] is well documented.

Similarly, tautomeric equilibria involving protonation at the 3-position have been observed previously.[7] The fact that the 3- and 5-positions are conjugated is crucial to this mechanism and explains the difference between these reactions and those of the analogous *peri*-substituted naphthalenes.

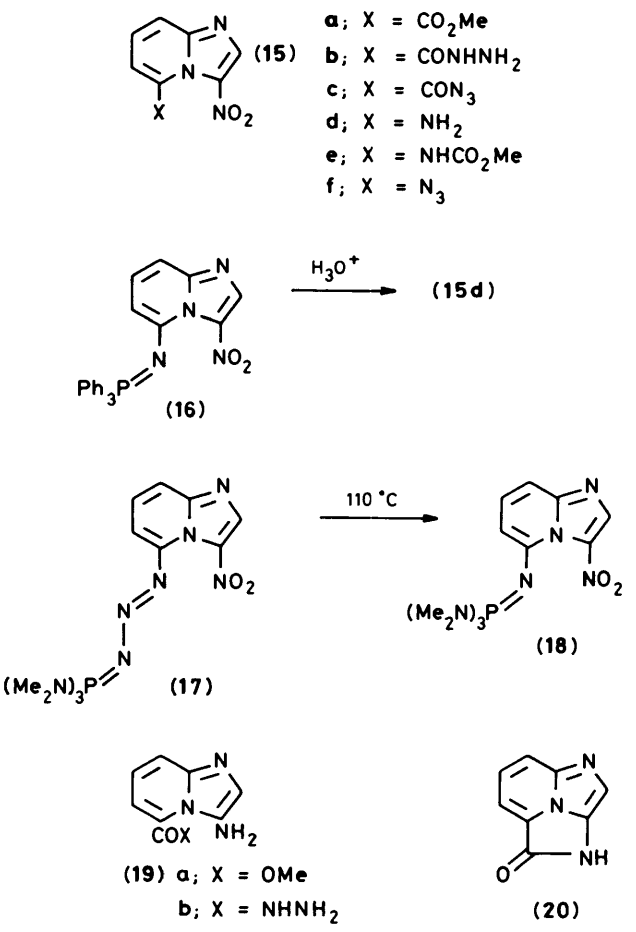
The unusual reaction of Scheme 3 bears a strong resemblance to an unexplained result in the literature:[8] whilst attempting to prepare a compound previously reported to be 1,3,5-trihydrazino-2,4,6-trinitrobenzene from 1,3,5-trichloro-2,4,6-trinitrobenzene (**9**), the unexpected dihydrazine (**12**) was isolated, together with the monohydrazine (**11**), under conditions similar to ours. The authors proposed the sequence (**9**) ⟶ (**10**) ⟶ (**11**) ⟶ (**12**) but could not rationalise the initial loss of the chloro and nitro groups. We proposed a sequence (Scheme 4)



Scheme 4.

very similar to that in Scheme 3. It is notable that only 1,4-reduced products were observed, though 1,2-reduction is also possible, and that the 1,4-reduction occurs only once, normal nucleophilic substitution predominating thereafter. The former presumably results from the greater stability of *para* than *ortho* quinonoid structures, and the latter from the greater relief of steric strain when the hexasubstituted benzene (**13**) tautomerises to (**14**) than in the corresponding processes for the tetrasubstituted compounds (**11**) and (**12**).

In the course of this work some other '*peri*'-substituted imidazo[1,2-*a*]pyridines were investigated, as possible precursors to tricyclic systems related to triazacyclopentindene (**2**). Thus the 5-methoxycarbonyl derivative was prepared by cyclisation of methyl 6-aminopyridine-2-carboxylate[9] with bromoacetaldehyde; treatment of the ester with nitric and sulphuric acids gave the 3-nitro derivative (**15a**) in high yield, though the reaction is sensitive to concentration.[10] Ester (**15a**) with hydrazine gave hydrazide (**15b**) which with nitrous acid gave the acyl azide (**15c**) and this in turn gave amide (**15d**) on heating in aqueous acetonitrile, and urethane (**15e**) on heating in methanolic benzene, all in high yield. 5-Bromoimidazo[1,2-*a*]-



pyridine (**6**) was prepared by cyclisation of 2-amino-6-bromopyridine[11] with bromoacetaldehyde, and nitrated to give the 3-nitro derivative (**7b**) which was smoothly converted into the 5-azide (**15f**).

Treatment of the azide (**15f**) with triphenylphosphine gave, with slow evolution of nitrogen, the iminophosphorane (**16**), whilst hexamethylphosphorous triamide gave the adduct (**17**) which was thermally much more stable than the analogous intermediate in the triphenylphosphine reaction. The adduct (**17**) could be recrystallised from benzene, though it lost nitrogen in boiling toluene to give compound (**18**). Presumably extensive electron delocalisation from the tris(dimethylamino)-phosphorous group to the nitroimidazopyridine ring stabilises the molecule towards nitrogen extrusion. Hydrolysis of the iminophosphorane (**16**) to the nitro amine (**15d**) provides a better route to this compound than the Curtius sequence above.

Based upon the cyclisation reactions of *ortho*-substituted nitrobenzenes[12] and of *peri*-substituted nitronaphthalenes,[1,2] we made many attempts to construct a third heterocyclic ring on the imidazopyridine by coupling of these various nitrogen linked 3,5-substituents, but all were unsuccessful.

Reduction of the nitro ester (**15a**) with hydrazine and palladium gave the aminocarboxyhydrazide (**19b**); the amino ester (**19a**) was obtained by reduction with iron and hydrochloric acid, though a hydrolysis product, methyl 6-aminopyridine-2-carboxylate, was also formed. The amino ester (**19a**) was cyclised to the lactam (**20**) by treatment with sodium methoxide in boiling methanol, but not by heating alone in toluene. Reduction of the bromo nitro compound (**7b**) with iron and hydrochloric acid gave low yields of the ring-opened products, 2-amino-6-bromopyridine and 2-bromo-6-(cyanomethyl-

amino)pyridine only. Analogous products have been observed in the catalytic hydrogenation of 3-nitrosoindolizines.[13]

Experimental

I.r. spectra were recorded for Nujol mulls on a Perkin-Elmer 257 spectrometer. N.m.r. spectra were recorded on a Perkin-Elmer R32 or Bruker WM 250 machine in deuteriochloroform ($CDCl_3$) or [$^2H_6$]dimethyl sulphoxide ([$^2H_6$]DMSO).

Organic extracts were dried with anhydrous magnesium sulphate. Column chromatography was on Merck Kieselgel H (type 60), unless stated otherwise, using hand bellows pressure. Known products were identified by direct comparison of n.m.r., i.r., and mass spectra, and by mixture m.p.s. for solids.

Ethyl 5-Methyl-3,5-dinitroimidazo[1,2-a]*pyridine-2-carboxylate* (**4**) *and Hydrazine.*—Compound (**4**) was prepared by the literature method[4] except that ethyl 6-methylimidazo[1,2-a]-pyridine was dissolved in a mixture of concentrated sulphuric acid (2 parts by vol.) and fuming nitric acid (*d* 1.5; 1 part by vol.). The mixture was stored overnight and the literature[4] work-up procedure then gave yields of up to 30%. Compound (**4**) (560 mg) was dissolved in refluxing ethanol (30 ml) with stirring. Palladium on charcoal (10%; 200 mg) was added, at reflux under nitrogen, followed by hydrazine hydrate (0.5 ml). After 10 min the solution was filtered through Celite and evaporated. Subjecting the black residue to column chromatography gave ethyl 6-methylimidazo[1,2-*a*]pyridine-2-carboxylate (**5**) (110 mg, 30%), purified by sublimation at 50 °C, 0.02 mmHg, and identified by direct comparison with authentic material.[4]

Repetition of this reaction in the absence of palladium on charcoal gave the same product (77 mg, 21%).

Ethyl 3-Amino-6-methylimidazo[1,2-a]*pyridine-2-carboxylate.*—Ethyl 6-methyl-3-nitroimidazo[1,2-*a*]pyridine-2-carboxylate[4] (2.5 g) was subjected to the above procedure using ethanol (150 ml), palladium on charcoal (10%; 800 mg) and hydrazine hydrate (2 ml). After filtration through Celite the product was recrystallised twice from ethanol, insoluble material being discarded, to give golden yellow crystals of the *title compound* (1.1 g, 50%), m.p. 250 °C (Found: C, 60.3; H, 6.0; N, 19.2 $C_{11}H_{13}N_3O_2$ requires C, 60.3; H, 6.0; N, 19.2%); $\nu_{max.}$ 3 400, 3 140, 1 680, and 1 650 cm^{-1}; δ_H([$^2H_6$]DMSO) 8.0 (br, 5-H), 7.3 (d, 8-H), 7.0 (d, 7-H), 6.3 (br, exchangeable, NH_2), 4.3 (q, CH_2), 2.2 (s, Ar-Me), and 1.3 (t, Me); *m/z* 219 (M^+).

3,5-*Dibromoimidazo*[1,2-a]*pyridine* (**7a**) *and Hydrazine.*—Compound (**7a**) (110 mg) was dissolved in ethanol (50 ml) and in DMF (50 ml) in separate experiments. Hydrazine hydrate (1.0 ml) was added to each and the solutions were heated under nitrogen. The ethanol solution was heated to reflux for 12 h and the DMF solution was heated at 110 °C for 30 min. The solutions were poured into water (100 ml) and extracted with ether. The ether solutions were dried and evaporated and the residual oils were chromatographed on silica gel. Elution with ether gave starting material (**7a**) (43 mg, 39% from the ethanol solution; 26 mg, 24% from the DMF solution). Elution with ethyl acetate gave imidazo[1,2-*a*]pyridine (**8**) (16 mg, 34% from the ethanol solution; 15 mg, 31% from the DMF solution).

5-*Bromo-3-nitroimidazo*[1,2-a]*pyridine* (**7b**) *and Hydrazine.*—Compound (**7b**) (100 mg) was dissolved separately in ethanol (50 ml) and DMF (50 ml) and treated with hydrazine hydrate (1.0 ml) as for compound (**7a**) above, except that the ethanol solution was refluxed for only 30 min. Work-up as for the experiments with (**7a**) gave imidazo[1,2-*a*]pyridine (**8**) (10 mg, 20% in each experiment). No starting material was recovered, the major products being unstable tarry materials.

Methyl Imidazo[1,2-a]*pyridine-5-carboxylate.*—Methyl 6-aminopyridine-2-carboxylate was prepared from 2-amino-6-methylpyridine by the literature method;[9] performing the esterification in methanol and sulphuric acid (80% yield) instead of methanol and hydrogen chloride (50% yield) gave the product in 28% overall yield.

Bromoacetaldehyde diethylacetal (8.0 g, 41 mmol) in hydrochloric acid (50%, 4 ml) was heated under reflux for 3 h. The mixture was poured into ethanol (30 ml) containing sodium hydrogen carbonate (4 g) and stirred for 1 h. The mixture was filtered and added to a solution of methyl 6-aminopyridine-2-carboxylate (4.2 g, 28 mmol) in ethanol (30 ml) containing sodium hydrogen carbonate (3 g). The mixture was stirred and refluxed for 16 h and then poured into saturated aqueous sodium hydrogen carbonate (200 ml) and extracted with dichloromethane. The combined extracts were concentrated under reduced pressure and the resultant black oil was subjected to column chromatography. Elution with light petroleum (b.p. 40—60 °C) gave aliphatic material and elution with ether then gave the title ester (2.45 g, 50%) sufficiently pure for further use. Recrystallisation from light petroleum (b.p. 80—100 °C) gave yellow crystals of the *ester*, m.p. 103—104 °C (Found: C, 61.1; H, 4.5; N, 15.75. $C_9H_8N_2O_2$ requires C, 61.4; H, 4.6; N, 15.9%); $\nu_{max.}$ 1 715 cm^{-1}; $\delta_H(CDCl_3)$ 8.8 (d, 3-H), 7.7 (m, 3 H), 7.1 (t, 7-H), and 4.0 (Me); *m/z* 176 (M^+).

Methyl 3-Nitroimidazo[1,2-a]*pyridine-5-carboxylate* (**15a**).—The above ester (4.5 g, 25.6 mmol) was dissolved in concentrated sulphuric acid (450 ml) and a 2:1 mixture of concentrated sulphuric acid and fuming nitric acid (7.0 ml) was added. The mixture was stored overnight and then poured into water (2.5 l) and extracted with dichloromethane (5 × 200 ml) to give the *nitro ester* (**15a**) (4.4 g, 80%), m.p. 110—111 °C (from ethanol) (Found: C, 48.7; H. 3.2; 19.2. $C_9H_7N_3O_4$ requires C, 48.9; H, 3.2; N, 19.0%); $\nu_{max.}$ 1 715 cm^{-1}; $\delta_H(CDCl_3)$ 8.55 (s, 2-H), 8.0 (t, 7-H), 7.7 (d, 2 H), and 4.0 (Me); *m/z* 221 (M^+) and 175 ($M^+ - NO_2$).

3-*Nitroimidazo*[1,2-a]*pyridine-5-carbohydrazide* (**15b**).—The nitro ester (**15a**) (750 mg) was dissolved in methanol (35 ml); hydrazine hydrate (2 ml) was added and the mixture heated under reflux for 3 h. The solution was reduced in volume (to *ca.* 10 ml) and left to cool. The crystals were collected as pure *carbohydrazide* (**15b**) (590 mg, 78%), m.p. 209 °C (decomp.) (Found: C, 43.7; H, 3.2; N, 31.4. $C_8H_7N_5O_3$ requires C, 43.4; H, 3.2; N, 31.7%); $\nu_{max.}$ 3 320, 3 200, and 1 665 cm^{-1}; δ_H([$^2H_6$]DMSO) 10.5 (br, exchangeable, CONH), 8.7 (s, 2-H), 8.1 (d, 1 H), 7.9 (t, 7-H), 7.1 (d, 1 H), and 4.6 (br, exchangeable, NH_2); *m/z* 221 (M^+) and 175 ($M^+ - NO_2$).

3-*Nitroimidazo*[1,2-a]*pyridine-5-carbonylazide* (**15c**).—The carbohydrazide (**15b**) (490 mg, 2.2 mmol) dissolved in hydrochloric acid (20%; 40 ml) was cooled to 0 °C, and a solution of sodium nitrite (165 mg, 2.4 mmol) in water (2 ml) was added. As the mixture warmed to room temperature a yellow precipitate formed and was collected as the pure *carbonylazide* (**15c**). The solution was also extracted with dichloromethane to give a combined yield of product of 490 mg (90%), m.p. 80 °C (decomp.) (Found: C, 41.4; H, 1.8; N, 36.1. $C_8H_4N_6O_3$ requires C, 41.4; H, 1.7; N, 36.2%); $\nu_{max.}$ 2 160br, and 1 680 cm^{-1}; $\delta_H(CDCl_3)$ 8.6, (s, 2-H), 8.1 (t, 7-H), and 7.7 (m, 2 H).

5-*Amino-3-nitroimidazo*[1,2-a]*pyridine* (**15d**).—The carbonylazide (**15c**) (400 mg) was dissolved in acetonitrile (25 ml) and water (0.5 ml) was added. The mixture was heated under reflux for 1 h. The solution was diluted with dichloromethane (100 ml), dried, and evaporated to give intense red needles (from ethanol) of the *nitro amine* (**15d**) (90%), m.p. 198—199 °C

(Found: C, 47.4; H, 3.4; N, 31.6. $C_7H_6N_4O_2$ requires C, 47.2; H, 3.4; N, 31.45%); $\nu_{max.}$ 3 320, 3 260, and 1 660 cm^{-1}; δ_H ($CDCl_3$, [$^2H_6$]DMSO) 8.7 (s, 2-H), 7.7 (t, 7-H), 7.4 (br, exchangeable, NH_2), 7.1 (d, 1 H), and 6.7 (d, 1 H); *m/z* 178 (M^+) and 132 ($M^+ - NO_2$).

Methyl 3-Nitroimidazo[1,2-a]*pyridin-5-ylcarbamate* (**15c**).—The carbonylazide (**15c**) (440 mg) was heated under reflux in benzene (20 ml) and methanol (5 ml) for 1.5 h and worked up as in the last experiment to give the *title compound* (410 mg, 91%) as golden red flakes (from methanol), m.p. 141—142 °C (Found: C, 46.0; H, 3.4; N, 23.8. $C_9H_8N_4O_4$ requires C, 45.8; H, 3.4; N, 23.7%); $\nu_{max.}$ 1 740 cm^{-1}; $\delta_H(CDCl_3)$ 10.0 (br, exchangeable, NH), 8.7 (s, 2-H), 7.9 (d, 1 H), 7.8 (t, 7-H), 7.5 (d, 1 H), and 3.88 (s, Me); *m/z* 236 (M^+) and 190 ($M^+ - NO_2$).

5-Bromoimidazo[1,2-a]*pyridine* (**6**).—2-Amino-6-bromopyridine[11] (8.5 g, 49 mmol) was heated under reflux for 6 h in an ethanol solution of bromoacetaldehyde generated from its diethyl acetal (19.7 g, 100 mmol) (as described above). The ethanol was removed under reduced pressure, 20% hydrochloric acid (100 ml) was added to the residue and the solution was then neutralised with aqueous sodium hydroxide and extracted with ether. The ether solution was dried and evaporated to give the *title compound* (**6**) (7.8 g, 79%) sufficiently pure for further use. Sublimation at 50 °C and 0.02 mmHg gave the pure compound which was unstable to storage, m.p. 61—64 °C (Found: C, 42.3; H, 2.45; N, 14.0. $C_7H_5BrN_2$ requires C, 42.6; H, 2.5; N, 14.2%); $\delta_H(CDCl_3)$ 7.7 (m, 3 H) and 7.1 (m, 2 H); *m/z* 198 (M^+) and 196 (M^+).

3,5-*Dibromoimidazo*[1,2-a]*pyridine* (**7a**).—The bromo compound (**6**) (585 mg, 3.0 mmol) was dissolved in dichloromethane (150 ml) and a solution of *N*-bromosuccinimide (540 mg, 3.0 mmol) in chloroform (50 ml) was added, and the mixture kept at room temperature overnight. It was then washed with 10% aqueous sodium hydroxide (20 ml) and water (20 ml) and the organic phase was dried and evaporated under reduced pressure. The residue (814 mg, 99%) was crystallised from light petroleum (b.p. 60—80%) to give the *title compound* (**7a**) as tan crystals (650 mg, 80%), m.p. 97—98 °C (Found: C, 30.55; H, 1.4; N, 10.1. $C_7H_4Br_2N_2$ requires C, 30.5; H, 1.5; N, 10.15%); $\delta_H(CDCl_3)$ 7.6 (m, 2 H), and 7.1 (m, 2 H); *m/z* 278 (M^+), 276 (M^+), and 274 (M^+).

5-Bromo-3-nitroimidazo[1,2-a]*pyridine* (**7b**).—Nitration of the bromo compound (**6**) (9.6 g) by the same method as in the preparation of nitro-ester (**15a**) above gave the *title compound* (**7b**) (10.7 g, 90%) as yellow plates (from ethanol), m.p. 160—161 °C (Found: C, 34.7; H, 1.5; N, 17.2. $C_7H_4BrN_3O_2$ requires C, 34.7; H, 1.6; N, 17.3%); $\delta_H(CDCl_3)$ 8.45 (s, 2-H), 7.9 (t, 7-H), and 7.6 (m, 2 H); *m/z* 243 (M^+), 241 (M^+), 197 ($M^+ - NO_2$), and 195 ($M^+ - NO_2$).

5-Azido-3-nitroimidazo[1,2-a]*pyridine* (**15f**).—The bromonitroimidazopyridine (**7b**) (480 mg, 1.95 mmol) was dissolved in dry DMF (25 ml), sodium azide (200 mg, 3.0 mmol) was added, and the mixture was stirred for 3.5 h. The brown solution was then poured into water (150 ml), extracted with ether, and the ether extracts were washed with water, dried, and evaporated. The *azide* (**15f**) was obtained as a yellow solid (350 mg, 87%), unstable on prolonged storage and resistant to recrystallisation. Sublimation at 100 °C, 0.07 mmHg gave a solid, m.p. 128 °C (decomp.) (Found: C, 41.6; H, 1.9. $C_7H_4N_6O_2$ requires C, 41.2; H, 1.9%); $\nu_{max.}$ 2 150, 2 130, and 2 100 cm^{-1}; $\delta_H(CDCl_3)$ 8.45 (s, 2-H), 7.7 (m, 2 H), and 7.0 (d, 1 H).

3-Nitro-5-tris(dimethylamino)phosphoranylidenetriazenoimidazo[1,2-a]*pyridine* (**17**).—The nitro azide (**15f**) (190 mg, 0.93 mmol) was dissolved in benzene (10 ml) and hexamethylphosphorous triamide (160 mg, 0.95 mmol) was added. The mixture was stirred for 2 min and then most of the benzene was removed by distillation. Crystals (260 mg, 76%) were collected on cooling, and recrystallised from benzene–light petroleum (b.p. 60—80 °C) to give yellow crystals of the *title compound* (**17**), m.p. 146—147 °C (decomp.) (Found: C, 42.8; H, 6.0; N, 34.4; P, 8.6. $C_{13}H_{22}N_9O_2P$ requires C, 42.5; H, 6.0; N, 34.3; P, 8.4%); $\nu_{max.}$ 1 210, 950 cm^{-1}; $\delta_H(CDCl_3)$ 8.45 (s, 2-H), 7.5 (m, 2 H), 7.0 (d, 1 H), and 2.8 (d, 18 H, *J* 9 Hz); *m/z* 368 (M^+ + 1), 367 (M^+), 339 ($M^+ - N_2$), and 293 ($M^+ - N_2 - NO_2$).

3-Nitro-5-tris(dimethylamino)phosphoranylideneaminoimidazo[1,2-a]*pyridine* (**18**).—The phosphatriazene (**17**) (370 mg) was heated under reflux in toluene for 1 h. The solvent was removed under reduced pressure and the residue recrystallised from benzene–light petroleum (b.p. 60—80 °C) to give red crystals of the *title compound* (**18**) (272 mg, 80%), m.p. 169—170 °C (Found: C, 45.9; H, 6.5; N, 28.8. $C_{13}H_{22}N_7O_2P$ requires C, 46.0; H, 6.5; N, 28.9%) $\delta_H(CDCl_2)$ 8.4 (s, 2-H), 7.4 (t, 7-H), 7.0 (d, 1 H), 6.2 (d, 1 H), and 2.75 (d, 18 H, *J* 9 Hz); *m/z* 339 (M^+) and 293 ($M^+ - NO_2$).

3-Nitro-5-triphenylphosphoranylideneimidazo[1,2-a]*pyridine* (**16**).—The nitro azide (**15f**) (447 mg, 2.2 mmol was dissolved in dichloromethane (10 ml) and a solution of triphenylphosphine (580 mg, 2.2 mmol) in dichloromethane (10 ml) was added. An instantaneous colour change was followed by slow evolution of nitrogen. After 16 h the solvent was removed under reduced pressure and the residue recrystallised from ethyl acetate to give red crystals of the *title compound* (**16**) (954 mg, 95%), m.p. 201—202 °C (Found: C, 68.5; H, 4.3; N, 12.8; P, 7.1. $C_{25}H_{19}N_4O_2P$ requires C, 68.5; H, 4.3; N, 12.7; P, 7.0%); $\delta_H(CDCl_3)$ 8.4 (s, 2-H), 8.0—6.9 (m, 17 H), and 5.8 (d, 1 H); *m/z* 438 (M^+) and 392 ($M^+ + NO_2$).

Hydrolysis of Compound (**16**).—Compound (**16**) (96 mg) was heated under reflux in a mixture of water (10 ml), methanol (30 ml), and concentrated hydrochloric acid (1 ml). After 2 h the solution was poured into aqueous sodium hydrogen carbonate and extracted thoroughly with dichloromethane. The organic layer was dried and evaporated to give the amine (**15d**) (30 mg, 77%) identical with that described above.

3-Aminoimidazo[1,2-a]*pyridine-5-carbohydrazide* (**19b**).—Methyl 3-nitroimidazo[1,2-a]pyridine-5-carboxylate (**15a**) (323 mg) was dissolved in ethanol (15 ml) heated at reflux under nitrogen; palladium on charcoal (10%; 60 mg) was added, followed rapidly by hydrazine hydrate (1.5 ml). The mixture was refluxed for 15 min and then filtered through Celite, and the filtrate evaporated to low volume and allowed to cool. Yellow crystals of the *title compound* (200 mg, 72%) were collected and recrystallised from ethanol, m.p. 188—190 °C (Found: C, 50.5; H, 4.7; N, 36.7. $C_8H_9N_5O$ requires C, 50.3; H, 4.7; N, 36.6%); $\nu_{max.}$ 3 350—3 100 and 1 600br cm^{-1}; δ_H([$^2H_6$]DMSO) 10.2 (br, exchangeable, NHCO), 7.6 (t, 7-H), 7.1 (m, 3 H), and 4.8 (br, exchangeable, 4 × NH); *m/z* 191 (M^+).

Methyl 3-Aminoimidazo[1,2-a]*pyridine-5-carboxylate* (**19a**).—The nitro ester (**15a**) (650 mg) was dissolved in methanol (40 ml), and iron (800 mg) followed by concentrated hydrochloric acid (2 ml) was added. The mixture was heated under reflux for 40 min, under nitrogen, and then poured into aqueous sodium hydrogen carbonate (100 ml). The brown mixture was filtered through Celite and extracted with dichloromethane. The organic layer was dried, evaporated to

dryness, and the residual red oil (420 mg) was chromatographed. Elution with (i) dichloromethane gave impurities, (ii) ether gave methyl 6-aminopyridine-2-carboxylate (50 mg, 10%), and (iii) ethyl acetate gave the *title amine* (**19a**) (350 mg, 63%), recrystallised from ethyl acetate and light petroleum (b.p. 60—80 °C) as red crystals, m.p. 98—99 °C (Found: C, 56.6; H, 4.75; N, 21.9. $C_9H_9N_3O_2$ requires C, 56.6; H, 4.7; N, 22.0%); $\nu_{max.}$ 3 350—3 100, 1 705, and 1 630 cm^{-1}; $\delta_H(CDCl_3)$ 7.75 (d, 1 H), 7.55 (d, 1 H), 7.3 (s, 2-H), 7.0 (t, 7-H), 4.3 (br, exchangeable, NH_2), and 4.0 (s, Me); *m/z* 191 (M^+).

1,3,7b-*Triazacyclopent*[bc]*inden*-4(3H)-*one* (**20**).—The amino-ester (**19a**) (110 mg, 0.58 mmol) was dissolved in dry methanol (30 ml), a solution of sodium methoxide from sodium (27 mg, 1.2 mmol) and methanol (20 ml) was added, and the mixture was heated under reflux for 3 h. Ammonium chloride (100 mg) in water (20 ml) was then added and the mixture was continously extracted with dichloromethane overnight. The organic layer was then dried and evaporated to give impure triazacyclopentindenone (**20**) (55 mg, 56%) which could not be recrystallised but was sublimed at 120 °C, 0.2 mmHg; m.p. 330 °C (decomp.); $\nu_{max.}$ 3 200—2 300 and 1 700 cm^{-1}; $\delta_H([^2H_6]DMSO)$ 12.5 (br, exchangeable, NH), 8.1 (d, 1 H), 8.0 (d, 1 H), 7.8 (t, 6-H), and 7.7 (s, 2-H); *m/z* 159 (M^+).

Attempted Reduction of 5-*Bromo*-3-*nitroimidazo*[1,2-a]-*pyridine* (**7b**).—Compound (**7b**) (400 mg) was dissolved in methanol (50 ml) and iron (500 mg) and concentrated hydrochloric acid (1 ml) was added under nitrogen. The mixture was heated under reflux for 10 min and then poured into saturated aqueous sodium hydrogen carbonate (100 ml). Extraction with dichloromethane gave an oil (140 mg) which on chromatography (SiO_2, $CHCl_3$) gave (i) 2-*bromo*-6-(*cyanomethylamino*)-*pyridine* (17 mg, 5%) purified by sublimation (75 °C, 0.03 mmHg) and recrystallisation [light petroleum (b.p. 60—80 °C)] to give crystals, m.p. 84—85 °C (Found: C, 39.95; H, 2.8; N, 19.7. $C_7H_6BrN_3$ requires C, 39.65; H, 2.85; N, 19.8%); $\delta_H(CDCl_3)$ 7.4 (t, 4-H), 7.0 (d, 1 H), 6.5 (d, 1 H), 5.0 (br, exchangeable, NH), and 4.4 (d, CH_2; s on addition of D_2O); *m/z* 213 (M^+), 211; and (ii) 2-amino-6-bromopyridine (67 mg, 23%).

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Received 27*th June* 1986; *Paper* 6/1295