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Ring Contraction of 2-Azidopyridine 1-Oxides and Related Compounds.[1,2] 2-Cyano-1-hydroxypyrroles and -imidazoles

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Abstract: A series of 2-azidopyridine 1-oxides was prepared from the corresponding 2-aminopyridine 1-oxides, and their thermal decomposition in benzene, methanol, and aniline was studied. In benzene, decomposition occurred smoothly at 85–95° to give 2-cyano-1-hydroxypyrroles as the exclusive products in good yields. The decomposition of 3-substituted-2-azidopyridine 1-oxides led to 2-substituted-2-cyano-2*H*-pyrrole 1-oxides which readily formed 1:1 adducts with phenyl isocyanate. In methanol or aniline, 2-cyanopyrroles and 3-substituted-2,3-dihydro-2-pyrrolones were isolated involving nucleophilic addition of a solvent molecule to the open-chain intermediate. 2-Azidopyrazine 1-oxide in benzene gave 2-cyano-1-hydroxyimidazole. A possible mechanism is suggested which does not invoke the formation of a nitrene but involves a concerted elimination of nitrogen and ring opening followed by ring contraction.

The thermal and photochemical decomposition of 3- and 4-azidopyridine 1-oxides have been studied,[3,4] and the products obtained appear to result from nitrene intermediates. On the other hand, the chemistry of 2-azidopyridine 1-oxide (**3a**) has received little attention.[5] In a related study, Kamiya[6] observed that the decomposition of 6-azidopyridazine 1-oxide is faster than that of some 3-azidopyridazine 1-oxides, but the products were not isolated. In principle, the properties of the nitrene derived from **3a** could be modified appreciably from those expected of an electrophilic arylnitrene by the presence of the ortho *N*-oxide oxygen. For example, it could exhibit 1,4-dipole behavior (**4**). Alternatively, **3a** could undergo ring contraction with elimination of nitrogen, as has been observed for some cyclic azides.[7] This could involve formation of a nitrene (**4**) or be a concerted process, ring opening accompanying nitrogen elimination. With a view to deciding between these various possibilities, we prepared a series of 2-azidopyridine 1-oxides (**3a–h**) and investigated their thermal decomposition in benzene, methanol, aniline, and morpholine in one case. To date, we have not observed any 1,4-dipolar behavior but have observed ring contraction leading to 2-cyano-1-hydroxypyrroles.

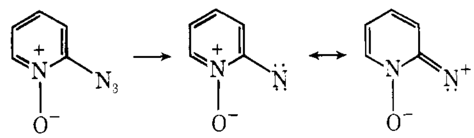
There is little known about *N*-hydroxypyrroles. The first example was prepared by Knorr[8a] who treated 3,4-dicarbethoxyhexa-2,5-dione with hydroxylamine to get 2,5-dimethyl-1-hydroxypyrrole-3,4-dicarboxylic ester. This was hydrolyzed and decarboxylated to 2,5-dimethyl-1-hydroxypyrrole. The same compounds were also prepared from di-

Table I. 2-Cyano-1-hydroxypyrroles (**6**) from the Thermolysis of **3** in Benzene

R in **3**	Dec temp, °C	Time, h	R in **6**	Yield, %	Mp [bp], °C	Calcd, %		Found, %	
						C	H	C	H
a, H	90	12	H	90	[80–82 (0.5 mm)]	*m/e*	108.0324[a]	*m/e*	108.0326
c, 4-CH_3	85	12	3-CH_3	44	56–58	59.01	4.92	59.32	5.05
d, 5-CH_3	85	8	4-CH_3	59	61–62	*m/e*	122.0480[b]	*m/e*	122.0480
e, 6-CH_3	90	8	5-CH_3	74	[103–105 (0.5 mm)]	59.01	4.92	59.12	5.04
f, 4,6-Me_2	90	12	3,5-Me_2	65	88–89	*m/e*	136[c]	*m/e*	136
g, 5-Cl	95	12	4-Cl	82	101–103	42.10	2.10	42.34	2.10

[a] Calcd for $C_5H_4N_2O$. [b] Calcd for $C_6H_6N_2O$. [c] Microanalytical data were obtained for the 1-benzoyloxy derivative (see Experimental Section).

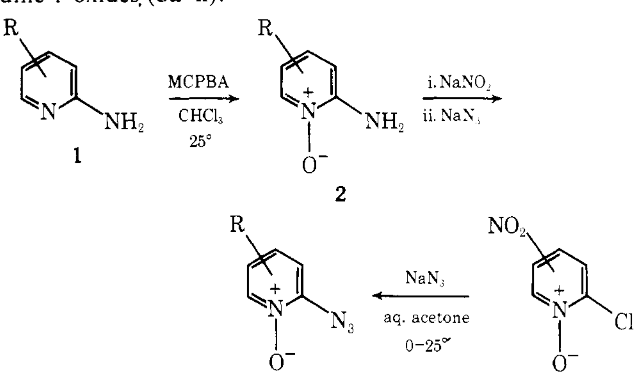
ethyl acetylmalonate.[8b] 2,3,5-Triphenyl-[8c] and 3-acetyl-2-methyl-5-phenyl-1-hydroxypyrrole[8d] were also prepared. The only reactions reported for the ring system are nitrosation with nitrous acid[8e] and deoxygenation with zinc and acetic acid.[8b]



3a **4**

Results and Discussion

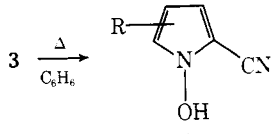
The direct oxidation of 2-aminopyridines (**1a–h**) to 2-aminopyridine 1-oxides (**2a–h**) with *m*-chloroperbenzoic acid (MCPBA) in chloroform by modification of Pentimalli's procedure,[9] followed by diazotization of the amine *N*-oxides and addition of sodium azide, gave the 2-azidopyridine 1-oxides (**3a–h**).



1 **2** **3** **5**

The preparation of some 2-azidopyridine 1-oxides (**3i–k**) from 2-halopyridine 1-oxides (**5a–c**) was also examined. Treatment of the known[10] 2-chloro-3-nitro- (**5a**) and 2-chloro-5-nitropyridine 1-oxide (**5b**) with excess sodium azide in aqueous acetone gave the corresponding 2-azido-3-nitro- (**3i**) and 2-azido-5-nitropyridine 1-oxides (**3j**) in yields of 41 and 80%, respectively. When 2-bromo-4-nitropyridine 1-oxide (**5c**)[11] was treated similarly, 2,4-diazidopyridine 1-oxide (**3k**) was obtained.[12] 2-Chloropyridine 1-oxides, not bearing a strongly electron-withdrawing substituent, reacted with azide ion at temperatures above those at which decomposition of **3** occurred.

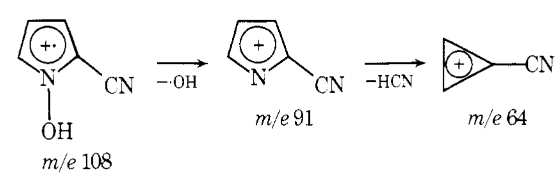
The thermal decomposition of 2-azidopyridine 1-oxides (**3a, c–g**) in degassed benzene occurred smoothly at 85–95° to give 2-cyano-1-hydroxypyrroles (**6a, c–g**) in high yields (Table I). The structure of these novel pyrroles followed



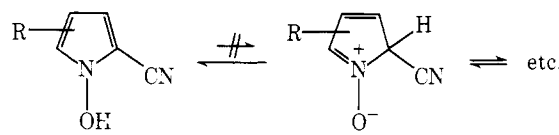
6

from their spectral properties and microanalysis. For example, **6a** exhibited a broad band between 3400 and 2800 cm^{-1} (NO-H) and a strong band at 2225 cm^{-1} (C≡N). Signals were present at δ 7.56 (1 H, br s, NOH) which disappeared on adding D_2O, 6.90 (1 H, d of d, $J_{4,5}$ = 2.5; $J_{3,5}$ = 1.5 Hz, H_5), 6.55 (1 H, d of d, $J_{3,4}$ = 3.5; $J_{3,5}$ = 1.5 Hz, H_3), and 5.96 (1 H, d of d, $J_{4,5}$ = 2.5; $J_{3,4}$ = 3.5 Hz, H_4). The mass spectrum showed the molecular ion at *m/e* 108 which was also the base peak. The major fragmentation involved loss of OH to give an ion at *m/e* 91, followed by elimination of HCN to give an ion at *m/e* 64. This could be accounted for as in Scheme I. The ^1H NMR spectra of *N*-

Scheme I

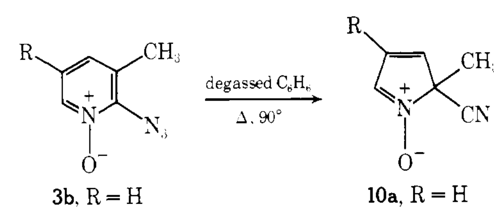


hydroxypyrroles (**6**) are collected in Table II. No evidence was found for the presence of any tautomeric modifications of **6** either in solid state or in solution. In addition, the *N*-



hydroxypyrroles (**6a,c–g**) formed *O*-*p*-toluenesulfonates (**7**), *O*-*p*-nitrobenzyl derivatives (**8**), and *O*-benzoates (**9**) readily, all of which exhibited the expected spectral properties.

Thermolysis of 2-azido-3-methylpyridine 1-oxides (**3b,h**) in benzene at 90° gave 2-cyano-2-methyl-2*H*-pyrrole 1-oxides (**10a,b**) in 89 and 77% yield, respectively. The proof of structure of these novel pyrrole *N*-oxides rests primarily on spectral and microanalytical evidence. Thus, the infrared spectrum of **10a** showed a nitrone band at 1525 cm^{-1} (cf.



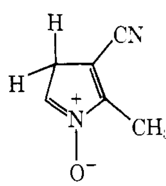
3b, R = H **10a**, R = H
h, R = Br **b**, R = Br

similar cyclic nitrones[13]). A film of the compound did not show a C≡N absorption, but one was present in the solution spectrum.[14] On the other hand, the NMR spectrum of the product in $CDCl_3$ solution seemed inconsistent with structure **10a** and exhibited a 1H low-field triplet at δ 7.7 (*J* = 2.5 Hz), a 2H doublet at δ 6.0 (*J* = 2.5 Hz), and a methyl 3H singlet at δ 1.82. Irradiation of the δ 6.0 signal caused the δ 7.7 one to collapse to a singlet, and the same

Table II. ^{1}H NMR Spectra of 2-Cyano-1-hydroxypyrroles (**6**) in $CDCl_3$

Substituent	δ				Hz			δ
	H_3	H_4	H_5	OH	$J_{3,4}$	$J_{3,5}$	$J_{4,5}$	Other
	6.55	5.96	6.90	7.56	3.5	1.5	2.5	
3-Me		5.90	6.80	8.07			4.0	Me, 2.10
4-Me	6.40		6.75	7.00		2.0		Me, 2.24
5-Me	6.55	5.80		7.80	5.5			Me, 2.20
3,5-Me_2		5.51		8.30				Me_2, 2.15, 2.03
4-Cl	6.50		6.90	7.50		2.0		

happened to the δ 6.0 one when the δ 7.7 one was irradiated. Addition of $Eu(fod)_3$ caused extensive shifts of all the peaks (the δ 7.7 peak suffered the greatest shift and must be due to the proton closest to the complexed *N*-oxide function), but no resolution of peak degeneracy occurred. Other possible structures, e.g., **11** and **12**, were considered but rejected as unlikely since they would have required the occurrence of multiple rearrangements and **12**, for example, is a tautomer of **6c** in which the *N*-hydroxy form is known to be the preferred (if not exclusive) tautomer.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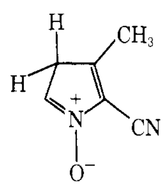
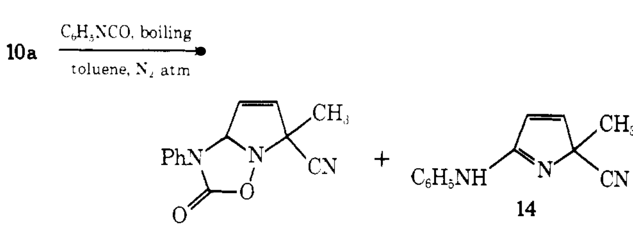

12

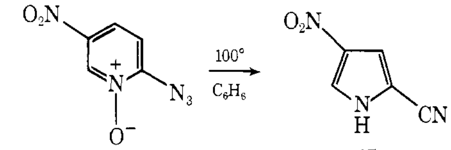
The ^{13}C NMR spectrum of **10a** resolved the problem and fitted that structure only: the nitrile carbon resonance occurred at 117.8 ppm (s), an indication that the C≡N group is bonded to an sp^3 carbon; the methyl group at C(2) gave rise to a quartet at 24.7 ppm, while the resonance for C(2) appeared as a singlet at 66.8 ppm, while C(5), C(4), and C(3) gave rise to doublets at 147.4, 116.8, and 129.4 ppm, respectively. Finally, the accidental degeneracy of H_3 and H_4 in $CDCl_3$ was lifted by measuring the NMR spectrum of **10a** in Me_2SO-d_6: H_5 gave rise to a doublet of doublets (δ 8.08, $J_{4,5}$ = 4 Hz; $J_{3,5}$ = 2 Hz), H_4 to a doublet of doublets (δ 6.24, $J_{4,5}$ = 4 Hz; $J_{3,4}$ = 10 Hz), and H_3 to a doublet of doublets at δ 6.39. The CH_3 group gave a sharp singlet at δ 1.81.

The nitrone structure of **10a** was also supported by its reaction with phenyl isocyanate in boiling toluene to give a 1:1 adduct (**13**) and 5-anilino-2-cyano-2-methyl-2*H*-pyrrole (**14**) in 16 and 11% yields, respectively, along with much tar. Elimination of carbon dioxide from pure **13** did not occur on boiling in chlorobenzene, probably because base catalysis is necessary for decarboxylation as has been shown for the adduct of 3-picoline 1-oxide and phenyl isocyanate.[15]



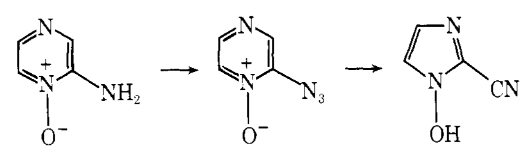
13 **14**

Thermolysis of 2-azido-5-nitropyridine 1-oxide (**3j**) in benzene did not give the expected 2-cyano-1-hydroxy-4-nitropyrrole, but yielded instead the deoxygenated product, 2-cyano-4-nitropyrrole (**15**).[16] The thermolysis of **3i** and **3j** in benzene gave only tar.



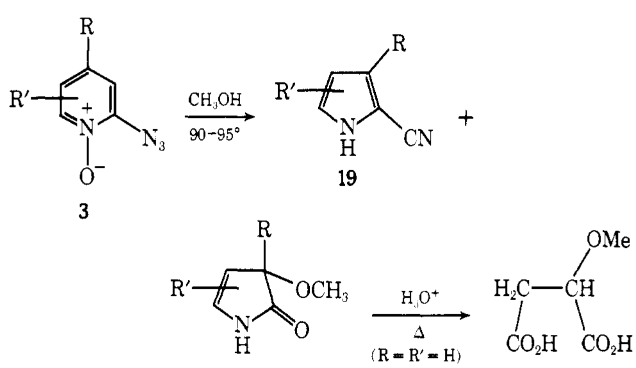
3j **15**

The known[17] 2-aminopyrazine 1-oxide (**16**) was converted to 2-azidopyrazine 1-oxide (**17**) in 25% yield. Thermolysis of **17** in benzene gave 2-cyano-1-hydroxyimidazole (**18**) in 83% yield whose structure followed from its spectra and microanalysis: ir (KBr) 2400 (v br, NOH) and 2225 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 7.80 (1 H, br s, NOH, exchangeable), 7.37 (1 H, d, $J_{4,5}$ = 3 Hz, H_5), 7.10 (1 H, d, $J_{4,5}$ = 3 Hz, H_4); *m/e* 109 ($M\cdot^+$).



16 **17** **18**

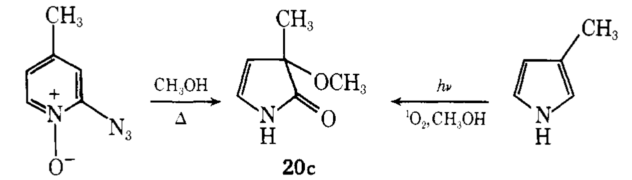
When the thermolysis of the azides (**3a,c,d,f,g**) was carried out in anhydrous degassed methanol, 2-cyanopyrroles (**19**)[18] and 3-methoxy-2,3-dihydro-2-pyrrolones (**20**) were



3 **19** **20** **21**

isolated. The former appears to arise by deoxygenation of the initially formed 2-cyano-*N*-hydroxypyrroles (**6**) in hot methanol. This was confirmed by heating **6** in methanol at 95° for 20 h to give **19**. It is assumed that the solvent undergoes oxidation, but no attempt was made to identify the oxidation product(s). The structures of **20** were suggested from their spectral properties. Thus, **20a** (R = R' = H) showed absorptions at 3260 (NH), 1690 (amide (C=O), and 1103 cm^{-1} (C-OCH_3). In $CDCl_3$ it exhibited signals at δ 7.78 (1 H, br s, NH, exchangeable), 6.84 (1 H, d of d, $J_{4,5}$ = 3.5; $J_{1,5}$ = 1 Hz, H_5), 6.08 (1 H, d of d, $J_{4,5}$ = $J_{1,4}$ = 0.5 Hz, H_4), 5.24 (1 H, s, H_3), and 3.24 (3 H, s, OCH_3). Its mass spectrum exhibited a molecular ion at *m/e* 113 and loss of OCH_3 to give a base peak at *m/e* 82. Further support for the structure of **20a** came from its hydrolysis to α-methoxysuccinic acid, (**21**).[19] The singlet oxygen photooxidation of

3-methylpyrrole gives a low yield of 3-methoxy-3-methyl-2,3-dihydro-2-pyrrolone (**20**) along with other products.[20] Thermolysis of 2-azido-4-methylpyridine 1-oxide (**3c**) in methanol gave, along with 2-cyano-3-methylpyrrole (**19c**), **20c** in 48% yield, identical with the product obtained by

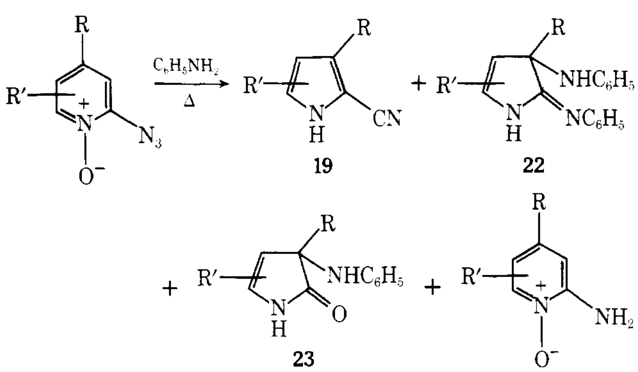


3c **20c**

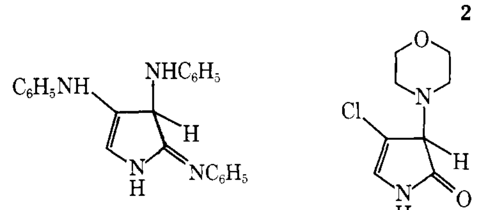
Lightner and Low.[20] Under these conditions, 2-azido-4,6-dimethylpyridine 1-oxide gave only 2-cyano-3,5-dimethylpyrrole.

When the thermolysis of the azides (**3a,c,d,g**) was carried out in aniline, 2-cyanopyrroles (**19**), either 2-anilino-2,3-dihydro-2-pyrrolone *N*-phenylimines (**22**) or 3-anilino-2,3-dihydro-2-pyrrolones (**23**), and 2-aminopyridine 1-oxides (**2**) were isolated. The infrared spectrum of **22a** exhibited a strong absorption at 1660 cm^{-1} characteristic of *N*-phenylimines.[21] NH stretching frequencies were observed at 3360 (anilino NH) and 3160 (amide NH) cm^{-1}. The NMR spectrum of **22a** exhibited resonances at δ 7.87 (1 H, br s, NH, exchangeable), 7.25 (5 H, m, phenyl H), 6.87 (5 H, m. phenyl H), 6.19 (d of d, 1 H, $J_{1,5}$ = 1.0 Hz; $J_{4,5}$ = 3.5 Hz, H_5), 6.02 (d of d, 1 H, $J_{1,4}$ = 0.5 Hz; $J_{4,5}$ = 3.5 Hz, H_4), 5.87 (1 H, s, H_3), and 4.05 (1 H, br s, NH, exchangeable). The mass spectrum had a molecular ion at *m/e* 250. When **22a** was heated in wet aniline at 100° it was recovered unchanged, but it slowly underwent hydrolysis in aqueous sodium hydroxide to **23a** [ν_{max} 3200 (amide NH), 1690 (C=O), 1625 cm^{-1} (C=C)].

In addition to 4-chloro-2-cyanopyrrole (**19g**) and 2-amino-5-chloropyridine 1-oxide (**2g**) the thermolysis of 2-azido-5-chloropyridine 1-oxide (**3g**) in aniline gave pyrrolone **22g** in which the chlorine atom had been replaced by an anilino group. On the other hand, it remained intact in the decomposition of **3g** in morpholine, and **24** was formed.



19 **22** **23** **2**



22g **24**

In some cases (e.g., **3c** and **3d**), no *N*-phenylimines (**22**) were obtained; instead, pyrrolones **23c** and **23d** were isolated in moderate yields, along with the expected 2-cyanopyrroles.

It has been calculated that 2-aminopyrrole is more stable in the amino- than in the imino-tautomeric form[22] and that it does not liberate ammonia with alkali.[23] Interestingly, however, compounds **22** (R = H) clearly prefer to exist in the imino modification.

In view of the mild conditions employed in the thermolysis (aryl azides do not undergo ready thermolysis much below 130° [7,24]) and the absence of nitrene products in hydrocarbon solvents, it is felt that a nitrene is not involved in the rearrangement. Also, none of the usual aryl nitrene products (amine or azo compounds) was isolated. Instead, a concerted elimination of nitrogen and ring opening is postulated to give the unsaturated nitrile (**25**) (Scheme II). In hydrocarbon solvents this can undergo electrocyclic ring closure to give the 2*H*-pyrrole *N*-oxide (**10**) (isolated when R = CH_3). When R = H, prototropic shift leads to the aromatic 2-cyano-1-hydroxypyrroles (**6**). In a nucleophilic solvent such as methanol, aniline, or morpholine, **25** (R = H) can undergo a Michael-type addition of the solvent, followed by cyclization and dehydration to give **26.** Readdition of water (or of alcohol when the reaction is carried out in methanol) followed by the elimination of RCN[25] would give 3-substituted 2,3-dihydro-2-pyrrolones (**20** and **23**). Indeed, the formation of 3-substituted 2-pyrrolones speaks strongly in favor of the intermediacy of a ring-opened product which then recyclizes. The apparent nitrene product, **2**, more likely arises by reduction of **25** to the hydroxylamine stage by aniline, followed by recyclization. Had a nitrene been an intermediate, one would have expected to isolate products derived therefrom in the thermolyses in methanol, but none was. An alternative possibility to the ring opening to **25** that we considered was an intramolecular cyclization to a pyridotriazole which could then ring contract following loss of nitrogen. There is, however, no precedent for the thermal formation of triazoles from aryl azides. Photoisomerization of PhN_3 does give a small amount of benzotriazole, but the latter is thermally stable. No pyridotriazole 7-oxides were detected,[27] so that we strongly favor the ring-opening ring-closure mechanism for which there are precedents, e.g., thermolysis of 2-azidotropone to give *o*-cyanophenol[28] and the thermolysis of azidoquinones.[29]

Experimental Section[30]

Materials. Bromination of 2-amino-3-methylpyridine (**1b**) according to a literature procedure[31] gave 2-amino-5-bromo-3-methylpyridine (**1h**), mp 91–93° (lit.[31] mp 90–92°). Oxidation of the 2-aminopyridines to 2-aminopyridine 1-oxides was carried out according to Pentimalli's procedure[9] except that *m*-chloroperbenzoic acid was used instead of perbenzoic acid.

2-Aminopyridine 1-oxide (**2a**) was prepared in 75% yield from **1a** and isolated as the hydrochloride, mp 158–159° (lit.[9] mp 158–160°).

2-Amino-3-methylpyridine 1-oxide (**2b**) was prepared in 94% yield from **1b.** Recrystallization from ethanol gave dull-yellow needles, mp 130–132° (lit.[32] mp 128–130°).

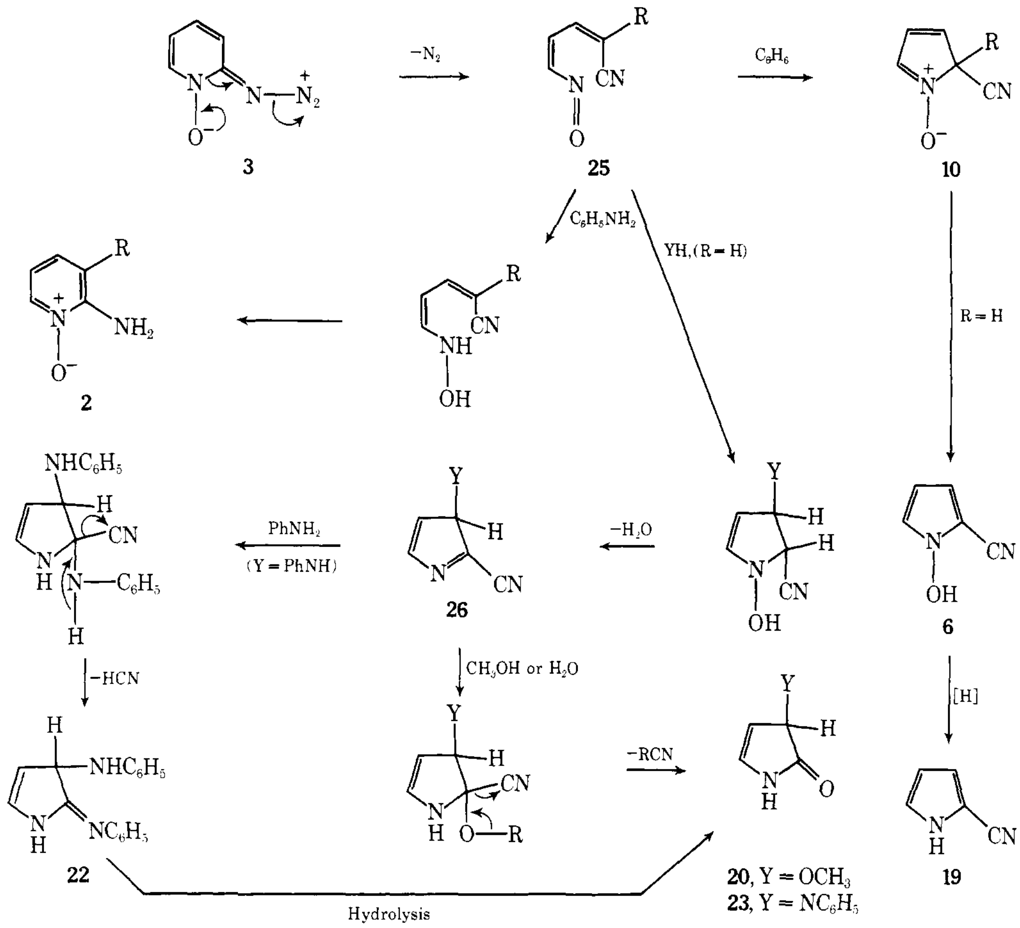
2-Amino-4-methylpyridine 1-oxide (**2c**) was prepared in 91% yield from **1c** and isolated as the hydrochloride, mp 176–178° (lit.[32] mp 175–177°).

2-Amino-5-methylpyridine 1-oxide (**2d**) was prepared in 88% yield from **1d** and isolated as the hydrochloride, mp 196–198° (lit.[33] mp 195–198°).

2-Amino-6-methylpyridine 1-oxide (**2e**) was prepared in 58% yield from **1e** and isolated as the hydrochloride, mp 214–216° (lit.[33] mp 212–214°).

2-Amino-4,6-dimethylpyridine 1-oxide (**2f**) was prepared in 70% yield from **1f** and isolated as the hydrochloride, mp 231–233° (lit.[32] mp 231°).

2-Amino-5-chloropyridine 1-oxide (**2g**) was prepared in 87% yield from **1g.** Recrystallization from 95% ethanol gave dull-yellow needles: mp 190–191°; ir (KBr) 3350, 3250 (NH_2) and 1235 cm^{-1} (*N*-oxide); NMR (acetone-d_6) δ 8.28 (d, 1 H, $J_{4,6}$ = 2.5 Hz, H_6), Scheme II



7.37 (d of d, 1 H, $J_{3,4}$ = 10 Hz; $J_{4,6}$ = 2.5 Hz, H_4), 7.04 (d, 1 H, $J_{3,4}$ = 10 Hz, H_3), and 6.50 (br s, 2 H, NH_2, exchanges with D_2O).

Anal. Calcd for $C_5H_5ClN_2O$: C, 41.52; H, 3.46. Found: C, 41.78; H, 3.61.

2-Amino-5-bromo-3-methylpyridine 1-oxide (2h) was prepared in 70% yield from **1h.** Recrystallization from benzene gave colorless needles: mp 152–153°; ir (KBr) 3300, 3200 (NH_2), and 1235 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 8.27 (d, 1 H, $J_{4,6}$ = 1.5 Hz, H_6), 7.85 (d, 1 H, $J_{4,6}$ = 1.5 Hz, H_4), 4.32 (br s, 2 H, NH_2, exchanges with D_2O), and 2.12 (s, 3 H, 3-CH_3).

Anal. Calcd for $C_6H_7BrN_2O{\cdot}H_2O$: C, 32.54; H, 4.09. Found: C, 32.64; H, 4.03.

General Procedure for the Preparation of 2-Azidopyridine 1-Oxides (3a–f) from 2-Aminopyridine 1-Oxides (2a–h). A vigorously stirred solution of the appropriate 2-aminopyridine 1-oxide or its hydrochloride in cold (0–5°) aqueous 10% hydrochloric acid was treated dropwise with an aqueous solution of sodium nitrite at such a rate that the temperature did not rise above 5°. An aqueous solution of sodium azide was then added dropwise, again maintaining the temperature below 5°. After stirring at 5° for 1 h, the solution was allowed to warm to room temperature and extracted with methylene chloride. Evaporation of the dried extracts on a rotary evaporator (bath temperature below 50°) gave the crude azides which were purified by recrystallization.

2-Azidopyridine 1-Oxide (3a) (70%): mp 83.5–84.5° dec [from petroleum ether–benzene (1:1 v/v)]; ir (KBr) 2175, 2160 (N_3), and 1250 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 8.05 (d of d, 1 H, $J_{5,6}$ = 1 Hz, H_6) and 7.02 (m 3 H, H_4, H_5).

Anal. Calcd for $C_5H_4N_4O$: C, 44.12; H, 2.96. Found: C, 44.37; H, 3.10.

2-Azido-3-methylpyridine 1-Oxide (3b) (72%): mp 89–90° dec [from hexane–benzene (1:1 v/v)]; ir (KBr) 2160 (N_3) and 1250 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 7.98 (d of d, 1 H, $J_{5,6}$ = 7 Hz; $J_{4,6}$ = 2 Hz, H_6), 6.97 (m, 2 H, H_4 and H_5), and 2.19 (s, 3 H, 3-CH_3).

Anal. Calcd for $C_6H_6N_4O$: C, 48.00; H, 4.00. Found: C, 48.18; H, 4.22.

2-Azido-4-methylpyridine 1-Oxide (3c) (80%): mp 54–56° dec; ir (KBr) 2170 (N_3) and 1250 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 7.95 (d, 1 H, $J_{5,6}$ = 5 Hz, H_6), 7.24 (d, 1 H, $J_{3,5}$ = 1 Hz, H_3), 6.75 (d of d, 1 H, $J_{5,6}$ = 5 Hz, $J_{3,5}$ = 1 Hz, H_5), and 2.28 (s, 3 H, 4-CH_3).

Anal. Calcd for $C_6H_6N_4O$: C, 48.00; H, 4.00. Found: C, 48.26; H, 4.15.

2-Azido-5-methylpyridine 1-Oxide (3d) (52%): mp 68–69° dec [from petroleum ether–benzene (2:1 v/v)]; ir (KBr) 2170 (N_3) and 1275 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 7.98 (d, 1 H, $J_{4,6}$ = 1.5 Hz, H_6), 7.05 (d of d, 1 H, $J_{3,4}$ = 7 Hz, $J_{4,6}$ = 1.5 Hz, H_4), 6.77 (d, 1 H, $J_{3,4}$ = 7 Hz, H_3), and 2.25 (s, 3 H, 5-CH_3).

Anal. Calcd for C_6H_6NO: C, 48.00; H, 4.00. Found: C, 48.26; H, 4.21.

2-Azido-6-methylpyridine 1-Oxide (3e) (72%): mp 43–46° dec [from petroleum ether–benzene (1:1 v/v)]; ir (KBr) 2160, 2140 (N_3), and 1250 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 7.00 (m, 3 H, H_3, H_4, and H_5) and 2.53 (s, 3 H, 6-CH_3).

Anal. Calcd for $C_6H_6N_4O$: C, 48.00; H, 4.00. Found: C, 48.18; H, 4.20.

2-Azido-4,6-dimethylpyridine 1-Oxide (3f) (60%): mp 96–98° dec [from chloroform–hexane (1:1 v/v)]; ir (KBr) 2150, 2120 (N_3), and 1250 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 6.82 (d, 1 H, $J_{3,5}$ = 2 Hz, H_3), 6.20 (d, 1 H, $J_{3,5}$ = 2 Hz, H_5), 2.43 (s, 3 H, 6-CH_3), and 2.22 (s, 3 H, 4-CH_3).

Anal. Calcd for $C_7H_8N_4O$: C, 51.22; H, 4.88. Found: C, 51.38; H, 4.95.

2-Azido-5-chloropyridine 1-Oxide (3g) (62%): mp 80–82° dec (from benzene); ir (KBr) 2175, 2160 (N_3), and 1255 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 8.16 (d, 1 H, $J_{4,6}$ = 1 Hz, H_6), 7.22 (d of d, 1 H, $J_{4,6}$ = 1 Hz; $H_{3,4}$ = 8 Hz, H_4), and 6.83 (d, 1 H, $J_{3,4}$ = 8 Hz, H_3).

Anal. Calcd for $C_5H_3ClN_4O$: C, 35.19; H, 1.76. Found: C, 35.12; H, 1.76.

2-Azido-5-bromo-3-methylpyridine 1-Oxide (3h) (25%): mp 96–98° dec [from hexane–benzene (1:1 v/v)]; ir (KBr) 2140, 2095 (N_3), and 1285 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 8.08 (d, 1 H, $J_{4,6}$ = 1 Hz, H_6), 7.14 (d, 1 H, H_4), and 2.12 (s, 3 H, 3-CH_3).

Anal. Calcd for $C_6H_5BrN_4O$: C, 31.44; H, 2.18. Found: C, 31.56; H, 2.23.

2-Azido-3-nitropyridine 1-Oxide (3i). A solution of 2-chloro-3-

nitropyridine 1-oxide (1.20 g, 7 mmol) and sodium azide (0.91 g, 14 mmol) in water (10 ml) and acetone (25 ml) was kept at 0° for 3 weeks. Removal of the acetone under reduced pressure and cooling gave **3i** (0.51 g, 41%) mp 85.5–87.5° dec (from benzene); ir (KBr) 2165 (N_3), 1530, 1352 (NO_2), and 1270 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 8.33 (d of d, 1 H, $J_{4,6}$ = 1.5 Hz, $J_{5,6}$ = 9 Hz, H_6), 7.75 (d of d, 1 H, $J_{4,6}$ = 1.5 Hz, $J_{4,5}$ = 3 Hz, H_4), and 7.20 (d of d, 1 H, $J_{5,6}$ = 9 Hz, $J_{4,5}$ = 3 Hz, H_5).

Anal. Calcd for $C_5H_3N_5O_3$: C, 33.15; H, 1.66. Found: C, 33.39; H, 1.86.

2-Azido-5-nitropyridine 1-Oxide (3j). A solution of 2-chloro-5-nitropyridine 1-oxide (2.50 g, 14 mmol) and sodium azide (2.00 g, 30 mmol) in water (40 ml) and acetone (140 ml) was stirred at room temperature for 48 h, then extracted with chloroform (3 × 50 ml). Evaporation of the dried chloroform extract and recrystallization from benzene gave pure **3j** (2.00 g, 80%): mp 118–119° dec; ir (KBr) 2170, 2130 (N_3), 1529, 1365 (NO_2), and 1270 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 8.50 (d, 1 H, $J_{4,6}$ = 2.5 Hz, H_6), 7.50 (d of d, 1 H, $J_{4,6}$ = 2.5 Hz; $H_{3,4}$ = 9 Hz, H_3), and 6.70 (d, 1 H, $J_{3,4}$ = 9 Hz, H_3).

Anal. Calcd for $C_5H_3N_5O_3$: C, 33.15; H, 1.66. Found: C, 33.12; H, 1.69.

2,4-Diazidopyridine 1-Oxide (3k). A solution of 2-bromo-4-nitropyridine 1-oxide (3.50 g, 0.016 mol) and sodium azide (7.00 g, 0.107 mol) in water (75 ml) and acetone (75 ml) was kept at room temperature in the dark for 3 weeks. Evaporation of the acetone in vacuo and cooling gave **3k** (1.52 g, 52%): mp 132° (detonation) (from ethanol); ir (KBr) 2150, 2000 (N_3), and 1250 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 8.13 (d, 1 H, $J_{5,6}$ = 7 Hz, H_6), 6.70 (d of d, 1 H, $J_{5,6}$ = 7 Hz; $J_{3,5}$ = 3 Hz, H_5), and 6.63 (d, 1 H, $J_{3,5}$ = 3 Hz, H_3).

Anal: Calcd for $C_5H_3N_7O$: C, 33.90; H, 1.70. Found: C, 33.88; H, 1.74.

2-Azidopyrazine 1-Oxide (15). A solution of 2-aminopyrazine 1-oxide (0.46 g, 4.2 mmol) in 20% aqueous hydrochloric acid (25 ml) was cooled to 0° in an ice-salt bath. To this was added dropwise a solution of sodium nitrite (0.29 g, 4.2 mmol) in water (5 ml), followed by a solution of sodium azide (0.27 g, 4.2 mmol) in water (5 ml). After warming to room temperature, the mixture was extracted with chloroform. Evaporation of the chloroform extract gave 2-azidopyrazine 1-oxide (0.14 g, 25%): mp 85–87° dec; ir (KBr) 2165, 2150 (N_3), and 1260 cm^{-1} (*N*-oxide); NMR ($CDCl_3$) δ 8.25 (d, 1 H, $J_{5,6}$ = 4.5 Hz, H_6), 8.16 (s, 1 H, H_3), and 8.08 (d, 1 H, $J_{5,6}$ = 4.5 Hz, H_5); mass spectrum (70 eV) *m/e* 137 ($M\cdot^+$); $C_4H_3N_5O$ requires *m/e* 137. Attempts to purify **15** by recrystallization led to its partial decomposition.

2-Cyano-1-hydroxypyrrole (6a). A degassed solution of 2-azidopyridine 1-oxide (1.07 g, 7.8 mmol) in benzene (20 ml) was heated in a sealed tube at 90° for 8 hr. Evaporation of the solvent and distillation of the residue gave 2-cyano-1-hydroxypyrrole (0.76 g, 90%): bp 80–82° (0.5 mm); ^{13}C NMR ($CDCl_3$) δ_C 100.5 (s, C_2), 112.9 (s, C≡N), 105.6 (d, C_5), 116.5 (d, C_3), 123.6 (d, C_4); mass spectrum (70 eV) *m/e* (rel abundance) 109 (8), 108 (100, $M\cdot^+$), 92 (20, $M\cdot^+$ − O), 91 (29, $M\cdot^+$ − OH), 80 (6), 79 (8), 65 (37), 64 (43), 55 (43), 54 (20), and 53 (58).

Anal. Calcd for $C_5H_4N_2O$: *m/e* 108.0324. Found: *m/e* 108.0326.

2-Cyano-1-(*p*-toluenesulfonyloxy)pyrrole (7a). A solution of 2-cyano-1-hydroxypyrrole (120 mg, 1.1 mmol), *p*-toluenesulfonyl chloride (414 mg, 2.2 mmol), and pyridine (0.5 ml) in dry methylene chloride (20 ml) was stirred at room temperature for 24 h, ice (3 g) was added, and the solution was stirred an additional 24 h. The solution was then washed with 20% aqueous hydrochloric acid, then with aqueous potassium carbonate. Evaporation of the dried methylene chloride solution gave colorless needles of **2-cyano-1-(-toluenesulfonyloxy)pyrrole** (0.26 g, 89%): mp 79.5–80.5° (from benzene); ir (KBr) 2222 (C≡N), and 1392, 1190 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.62 (d of d, A_2B_2, 4 H, J_o = 7 Hz, toluene protons), 7.03 (d of d, 1 H, $J_{3,5}$ = 2 Hz, $J_{3,4}$ = 3.5 Hz, H_5), 6.59 (d of d, 1 H, $J_{3,5}$ = 2 Hz, $J_{3,4}$ = 3.5 Hz, H_3), 6.14 (d of d, 1 H, $J_{3,4}$ = 3.5 Hz; $J_{4,5}$ = 3. Hz, H_4), and 2.49 (s, 3 H, *p*-CH_3); mass spectrum (70 eV) *m/e* (rel abundance) 262 (2.5, $M\cdot^+$), 155 (63), and 91 (100, $C_7H_7^+$).

Anal. Calcd for $C_{12}H_{10}N_2O_3S$: C, 54.92; H, 3.82. Found: C, 54.94; H, 4.04.

1-Benzoyloxy-2-cyanopyrrole (9a). A solution of 2-cyano-1-hydroxypyrrole (0.43 g, 3.9 mmol), benzoyl chloride (1.02 g, 7.3 mmol), and pyridine (1 ml) in benzene (50 ml) was boiled under reflux for 12 h. Water was added to hydrolyze any unreacted benzoyl chloride and stirring was continued for 12 h. The solution was diluted with chloroform, washed with 20% aqueous HCl (20 ml) and then with aqueous K_2CO_3. Evaporation of the organic solvents in vacuo gave 1-benzoyloxy-2-cyanopyrrole (0.51 g, 62%): mp 81–82° (from petroleum ether–benzene); ir (KBr) 2220 (C≡N) and 1780 cm^{-1} (ester C=O); NMR ($CDCl_3$) δ 8.02 (d of t, 2 H, $J_{o,m}$ = 7 Hz, $J_{o,p}$ = 1.5 Hz, phenyl ortho protons), 7.65 (m, 3 H, phenyl meta and para protons), 7.00 (d of d, 1 H, $J_{3,5}$ = 2 Hz, $J_{4,5}$ = 3 Hz, H_5), 6.78 (d of d, 1 H, $J_{3,5}$ = 2 Hz, $J_{3,4}$ = 3 Hz, H_3), and 6.25 (d of d, 1 H, $J_{3,4}$ = 3 Hz; $J_{4,5}$ = 3.5 Hz, H_4); mass spectrum (70 eV) *m/e* (rel abundance) 212 (1.5, $M\cdot^+$), 105 (100, $PhCO^+$).

Anal. Calcd for $C_{12}H_8N_2O_2$: C, 67.92; H, 3.78. Found: C, 67.98; H, 3.95.

2-Cyano-1-(*p*-nitrobenzyloxy)pyrrole (8a). A solution of 2-cyano-1-hydroxypyrrole (0.13 g, 1.2 mmol), *p*-nitrobenzyl chloride (0.43 g, 2.5 mmol), and pyridine (0.25 ml) in chloroform (25 ml) was stirred at room temperature for 48 h. A saturated aqueous solution of K_2CO_3 (10 ml) was added, stirring was continued for 24 h, and the solution was extracted with chloroform (3 × 20 ml). The dried chloroform extract was evaporated in vacuo to give a red oil (0.35 g) which was chromatographed on silica gel (30 g). Elution with chloroform gave 2-cyano-1-(*p*-nitrobenzyloxy)pyrrole (0.22 g, 75%): mp 69–70° dec (from petroleum ether–benzene); ir (KBr) 2220 (C≡N) and 1520, 1345 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 7.90 (d of d, A_2B_2, 4 H, J_o = 7 Hz, ArH), 6.70 (d of d, 1 H, $J_{3,5}$ = 2 Hz; $J_{4,5}$ = 3 Hz, H_5), 6.49 (d of d, 1 H, $J_{3,5}$ = 2 Hz, $J_{3,4}$ = 3.5 Hz, H_3), 6.03 (d of d, 1 H, $J_{3,4}$ = 3.5 Hz, $J_{4,5}$ = 3 Hz, H_4), and 5.34 (s, 2 H, CH_2); mass spectrum (70 eV) *m/e* 243 ($M\cdot^+$).

Anal. Calcd for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.70. Found: C, 59.40; H, 3.88.

2-Cyano-1-hydroxy-3-methylpyrrole (6c). A degassed solution of 2-azido-4-methylpyridine 1-oxide (3.00 g, 0.02 mol) in dry benzene (40 ml) was heated in a sealed tube at 85° for 12 h. Evaporation of the solvent in vacuo gave 2-cyano-1-hydroxy-3-methylpyrrole (1.05 g, 43.5%): mp 58–60° (sublimation); ir (KBr) 3300–2800 (v br, NOH) and 2220 cm^{-1} (C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 123 (6, $M\cdot^+$ +1), 122 (70, $M\cdot^+$), 106 (54, M − O), and 105 (100, M − OH).

2-Cyano-3-methyl-1-(*p*-toluenesulfonyloxy)pyrrole (7c). A solution of 2-cyano-1-hydroxy-3-methylpyrrole (0.23 g, 1.8 mmol), *p*-toluenesulfonyl chloride (0.76 g, 3.9 mmol), and pyridine (0.25 ml) in dry methylene chloride (20 ml) was stirred at room temperature for 48 h. The reaction mixture was washed with 20% aqueous HCl (20 ml) and 10% aqueous K_2CO_3 (10 ml). The organic layer was dried and evaporated to give 2-cyano-3-methyl-1-(*p*-toluenesulfonyloxy)pyrrole (0.44 g, 89%): mp 72–73° (benzene); ir (KBr) 2220 (C≡N) and 1365, 1175 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.80–7.30 (d of d, A_2B_2, 4 H, J_o = 7 Hz, phenyl protons), 6.80 (d, 1 H, $J_{4,5}$ = 4 Hz, H_5), 5.95 (d, 1 H, $J_{4,5}$ = 4 Hz, H_4), 2.50 (s, 3 H, *p*-CH_3), and 2.10 (s, 3 H, 3-CH_3); mass spectrum (70 eV) *m/e* (rel abundance) 276 (3, $M\cdot^+$), 155 (72, $C_7H_7SO_2^+$), and 91 (100, $C_7H_7^+$).

Anal. Calcd for $C_{13}H_{12}N_2O_3S$: C, 56.52; H, 4.35. Found: C, 56.47; H, 4.49.

2-Cyano-1-hydroxy-4-methylpyrrole (6d). A degassed solution of 2-azido-5-methylpyridine 1-oxide (1.53 g, 0.01 mol) in benzene (30 ml) was heated in a sealed tube at 85° for 8 h. Evaporation of the solvent in vacuo gave 2-cyano-1-hydroxy-4-methylpyrrole (0.73 g, 59%): mp 61–62° (hexane); ir (KBr) 3290–2700 (v br, NOH) and 2220 cm^{-1} (C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 122 (70, $M\cdot^+$), 106 (51, $M\cdot^+$ − O), and 105 (100, $M\cdot^+$ − OH).

1-Benzoyloxy-2-cyano-4-methylpyrrole (9d). A solution of 2-cyano-1-hydroxy-4-methylpyrrole (1.50 g, 12 mmol) in 20% aqueous NaOH (25 ml) was treated with benzoyl chloride (3.38 g, 24 mmol). After stirring at room temperature for 30 min, the solution was extracted with $CHCl_3$ (3 × 50 ml). The dried extract was evaporated in vacuo to give 1-benzoyloxy-2-cyano-4-methylpyrrole (1.95 g, 75%): mp 69–70° (hexane); ir (KBr) 2235 (C≡N) and 1770 cm^{-1} (ester C=O); NMR ($CDCl_3$) δ 8.10 (d of t, 2 H, $J_{o,m}$ = 7 Hz, $J_{o,p}$ = 1.5 Hz, phenyl ortho protons), 7.53 (m, 3 H, phenyl meta and para protons), 6.72 (d, 1 H, $J_{3,5}$ = 1.5 Hz, H_5), 6.55 (d, 1 H, $J_{3,5}$ = 1.5 Hz, H_3), and 2.07 (s, 3 H, 4-CH_3); mass spectrum (70 eV) *m/e* (rel abundance) 227 (1.5, $M\cdot^+$) and 105 (100,

$C_6H_5CO^+$).

Anal. Calcd for $C_{13}H_{10}N_2O_2$: C, 69.01; H, 4.45. Found: C, 69.15; H, 4.53.

2-Cyano-1-hydroxy-5-methylpyrrole (6e). A degassed solution of 2-azido-6-methylpyridine 1-oxide (0.53 g, 3.5 mmol) in benzene (10 ml) was heated in a sealed tube at 90° for 8 h. Evaporation of the solvent in vacuo gave **2-cyano-1-hydroxy-5-methylpyrrole** (0.32 g, 74%): bp 103–105° (0.5 mm); ir (film) 3400–2600 (v br, NOH) and 2220 cm^{-1} (C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 122 ($M\cdot^+$, 100), 106 (15, M − O), and 105 (46, M − OH).

The **1-(*p*-toluenesulfonate**) [mp 59–61° (hexane)] was obtained as above in 50% yield: ir (KBr) 2220 (C≡N) and 1380, 1190 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.62 (d of d, A_2B_2, 4 H, phenyl protons), 6.54 (d, 1 H, $J_{3,4}$ = 5.5 Hz, H_3), 5.88 (d, 1 H, $J_{3,4}$ = 5.5 Hz, H_4), 2.49 (s, 3 H, *p*-CH_3), and 2.25 (s, 3 H, 5-CH_3); mass spectrum (70 eV) *m/e* 276 ($M\cdot^+$).

Anal. Calcd for $C_{13}H_{12}N_2O_3S$: C, 56.52; H, 4.35. Found: C, 56.78; H, 4.73.

The **1-(*p*-nitrobenzyloxy) derivative,** prepared as above, was chromatographed on silica gel (75 g). Elution with chloroform gave the product (45%): mp 80–81° (hexane); ir (KBr) 2220 (C≡N) and 1515, 1345 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 7.90 (d of d, A_2B_2, 4 H, phenyl protons), 6.54 (d, 1 H, $J_{3,4}$ = 5 Hz, H_3), 5.88 (d, 1 H, $J_{3,4}$ = 5 Hz, H_4), 5.37 (s, 2 H, OCH_2Ar), and 2.27 (s, 3 H, 5-CH_3); mass spectrum (70 eV) *m/e* 257 ($M\cdot^+$).

Anal. Calcd for $C_{13}H_{11}N_3O_3$: C, 60.70; H, 4.28. Found: C, 60.64; H, 4.47.

2-Cyano-3,5-dimethyl-1-hydroxypyrrole (6f). A degassed solution of 2-azido-4,6-dimethylpyridine 1-oxide (900 mg, 5.5 mmol) in benzene (20 ml) was heated in a sealed tube at 90° for 12 h. Evaporation of the solvent in vacuo gave 2-cyano-3,5-dimethyl-1-hydroxypyrrole (485 mg, 65%): mp 88–90° (hexane); ir (KBr) 3180 (NOH) and 2222 cm^{-1} (C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 136 (36, $M\cdot^+$), 121 (11, M − CH_3), 120 (21, M − O), and 119 (47, M − OH).

The **1-benzoyloxy derivative** (43%) [bp 195–198° (0.2 mm)] was prepared in the usual manner: ir (film) 2225 (C≡N) and 1775 cm^{-1} (ester C=O); NMR (CCl_4) δ 8.14 (m, 2 H, ortho protons), 7.52 (m, 3 H, meta and para protons), 5.72 (s, 1 H, H_4), 2.14 (s, 3 H, 5-CH_3), and 2.08 (s, 3 H, 3-CH_3); mass spectrum (70 eV) *m/e* 240 ($M\cdot^+$).

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 70.00; H, 5.00. Found: C, 69.75; H, 5.13.

4-Chloro-2-cyano-1-hydroxypyrrole (6g). A degassed solution of 2-azido-5-chloropyridine 1-oxide (873 mg, 5.1 mmol) in benzene (10 ml) was heated in a sealed tube at 95° for 12 h. Evaporation of the solvent gave 4-chloro-2-cyano-1-hydroxypyrrole (601 mg, 82%): mp 102–103° (benzene–hexane 1:1 v/v); ir (KBr) 3150 (NOH) and 2240 cm^{-1} (C≡N); mass spectrum (70 eV) *m/e* (rel abundance) 144 (10), 142 (30, $M\cdot^+$).

It gave a **1-*p*-toluenesulfonate** (0.69 g, 50%): mp 101–102° (benzene–hexane 1:1 v/v); ir (KBr) 2230 (C≡N) and 1395, 1178 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 7.80–7.30 (d of d, A_2B_2, 4 H, phenyl protons), 7.00 (d, 1 H, $J_{3,5}$ = 1.5 Hz, H_5), 6.46 (d, 1 H, $J_{3,5}$ = 1.5 Hz, H_3), and 2.50 (s, 3 H, *p*-CH_3); mass spectrum (70 eV) *m/e* 296, 298 ($M\cdot^+$).

Anal. Calcd for $C_{19}H_9ClN_2O_2S$: C, 48.23; H, 3.04. Found: C, 48.52; H, 3.12.

2-Cyano-2-methyl-2*H*-pyrrole 1-Oxide (10a). A degassed solution of 2-azido-3-methylpyridine 1-oxide (2.50 g, 0.0167 mol) in benzene (50 ml) was heated in a sealed tube at 90° for 8 h. Evaporation of the solvent and distillation of the residual oil gave 2-cyano-2-methyl-2*H*-pyrrole 1-oxide (1.82 g, 89%): bp 58–60° (0.06 mm); mass spectrum (70 eV) *m/e* 122 ($M\cdot^+$).

Anal. Calcd for $C_6H_6N_2O$: C, 59.01; H, 4.92. Found: C, 58.85; H, 5.06.

Reaction of 10a with Phenyl Isocyanate. A solution of 2-cyano-2-methyl-2*H*-pyrrole 1-oxide (1.80 g, 0.015 mol) and phenyl isocyanate (1.79 g, 0.015 mol) in toluene (100 ml) was boiled under reflux for 30 min. The solvent was removed in vacuo, and the residue was chromatographed on alumina (150 g). Elution with benzene gave the 1:1 adduct **13** (567 mg, 16%): mp 135–137° (hexane); ir (KBr) 2245 (C≡N) and 1745 cm^{-1} (C=O); NMR (Me_2SO-d_6) δ 7.63 (m, 6 H, phenyl protons and H_5), 6.26 (d of d, 1 H, $J_{3,4}$ = 10 Hz, $J_{4,5}$ = 1 Hz, H_4), 6.03 (d, 1 H, $J_{3,4}$ = 10 Hz, H_3), and 1.91 (s, 3 H, 2-CH_3); mass spectrum (70 eV) *m/e* (rel abundance) 241 (5, $M\cdot^+$), 196 ($M\cdot^+$ − CO_2), and 122 (100).

Anal. Calcd for $C_{13}H_{11}N_3O_2$: C, 64.74; H, 4.60. Found: C, 64.81; H, 4.76.

Elution with chloroform gave **5-anilino-2-cyano-2-methyl-2*H*-pyrrole (14)** (345 mg, 11%): mp 148–150° (hexane); ir (KBr) 3300 (NH), 2240 (C≡N), 1630 (C=N), and 1620 cm^{-1} (C=C); NMR ($CDCl_3$) δ 7.45 (m, 5 H, phenyl protons), 5.87 (d, 1 H, $J_{3,4}$ = 9 Hz, H_4), 5.58 (d, 1 H, $J_{3,4}$ = 9 Hz, H_3), 4.20 (br s, 1 H, NH, exchangeable), and 1.81 (s, 3 H, 2-CH_3); mass spectrum (70 eV) *m/e* 197 (22, $M\cdot^+$).

Anal. Calcd for $C_{12}H_{11}N_3$: C, 73.10; H, 5.63. Found: C, 73.31; H, 5.19.

4-Bromo-2-cyano-2-methyl-2*H*-pyrrole 1-Oxide (10b). A degassed solution of 2-azido-5-bromo-3-methylpyridine 1-oxide (1.46 g, 6.4 mmol) in benzene (30 ml) was heated in a sealed tube at 90° for 12 h. Evaporation of the solvent in vacuo gave 4-bromo-2-cyano-2-methyl-2*H*-pyrrole 1-oxide (980 mg, 77%): bp 125–127° (0.75 mm); ir (film) 2240 (C≡N), 1635 (C=N) and 1620 cm^{-1} (C=C); NMR (d_6-Me_2SO) δ 7.97 (d, 1 H, $J_{3,5}$ = 1 Hz, H_5), 6.48 (d, 1 H, $J_{3,5}$ = 1 Hz, H_3), and 1.83 (s, 3 H, 2-CH_3); *m/e* 202,200 (5, $M\cdot^+$).

Anal. Calcd for $C_6H_5BrN_2O$: C, 35.82; H, 2.48. Found: C, 36.08; H, 2.56.

2-Cyano-4-nitropyrrole (15). A degassed solution of 2-azido-5-nitropyridine 1-oxide (863 mg, 4.8 mmol) in benzene (20 ml) was heated in a sealed tube at 100° for 11 h. After cooling, an amorphous brown tar deposited from the solution and was filtered. Evaporation of the filtrate in vacuo gave 2-cyano-4-nitropyrrole (126 mg, 19%), mp 149–151° (lit.[15] mp 150–151°), identical with a sample kindly supplied by Dr. H. J. Anderson: ir (KBr) 3230 (NH), 2245 (C≡N), and 1510, 1365 cm^{-1} (NO_2); NMR ($CDCl_3$) δ 9.60 (br s, 1 H, NH, exchanges with D_2O), 8.20 (d, 1 H, $J_{3,5}$ = 2 Hz, H_5), and 7.60 (d, 1 H, $J_{3,5}$ = 2 Hz, H_3); mass spectrum (70 eV) *m/e* 137 ($M\cdot^+$).

2-Cyano-1-hydroxyimidazole (18). A degassed solution of 2-azidopyrazine 1-oxide (90 mg, 0.66 mmol) in dry benzene (10 ml) was heated in a sealed tube at 85° for 30 min. Upon cooling 2-cyano-1-hydroxyimidazole (60 mg, 83%): mp 169–171° dec; ir (KBr) 2400 (NOH) and 2235 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 7.80 (br s, 1 H, NOH, exchanged with D_2O), 7.37 (d, 1 H, $J_{4,5}$ = 3 Hz, H_5), and 7.10 (d, 1 H, $J_{4,5}$ = 3 Hz, H_4); mass spectrum (70 eV) *m/e* 109 (55, $M\cdot^+$), 93 (19), 92 (26), 40 (100).

Anal. Calcd for $C_4H_3N_3O$: C, 44.04; H, 2.75. Found: C, 44.17; H, 2.87.

Thermolysis of 2-Azidopyridine 1-Oxide in Methanol: 3-Methoxy-2,3-dihydro-2-pyrrolone (20a). A degassed solution of 2-azidopyridine 1-oxide (1.085 g, 8 mmol) in methanol (20 ml) was heated in a sealed tube at 95° for 18 h. Evaporation of the solvent at reduced pressure gave a red oil which was chromatographed on silica gel (50 g). Elution with benzene-chloroform (1:1 v/v) gave 2-cyanopyrrole (44 mg, 5%), bp 77° (0.05 mm) [lit.[16] bp 79° (0.06 mm)], identical with an authentic sample: ir (film) 3320 (NH) and 2230 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 9.40 (br s, 1 H, NH, exchanges with D_2O), 6.92 (d of d, 1 H, $J_{3,5}$ = 2 Hz, $J_{4,5}$ = 3 Hz, H_5), 6.70 (d of d, 1 H, $J_{3,5}$ = 2 Hz, $J_{3,4}$ = 3.5 Hz, H_3), and 6.15 (d of d, 1 H, $J_{4,5}$ = 3 Hz, $J_{3,4}$ = 3.5 Hz, H_4); mass spectrum (70 eV) *m/e* 92 ($M\cdot^+$).

Elution with chloroform-ether (1:1 v/v) gave **3-methoxy-2,3-dihydro-2-pyrrolone** (208 mg, 26%), mp 50–52° (sublimation).

Anal. Calcd for $C_5H_7NO_2$: C, 53.10; H, 6.20. Found: C, 52.94; H, 6.26.

Hydrolysis of 3-Methoxy-2,3-dihydro-2-pyrrolone. A solution of 3-methoxy-2,3-dihydro-2-pyrrolone (740 mg, 6.5 mmol) in 20% aqueous HCl (20 ml) was heated on a steam bath for 2 h. Extraction of the cooled reaction mixture with ether gave α-methoxysuccinic acid (185 mg, 20%), mp 106–107° (lit.[19] mp 106–108°).

Deoxygenation of 2-Cyano-1-hydroxypyrrole in Methanol. A degassed solution of 2-cyano-1-hydroxypyrrole (887 mg, 8 mmol) in absolute methanol (20 ml) was heated in a sealed tube at 95° for 20 h. Evaporation of the solvent and distillation of the residual oil gave 2-cyanopyrrole (625 mg, 85%), bp 81–82° (0.1 mm), identical with an authentic sample.

Thermolysis of 2-Azido-4-methylpyridine 1-Oxide in Methanol: 3-Methoxy-3-methyl-2,3-dihydro-2-pyrrolone (20c). A degassed solution of 2-azido-4-methylpyridine 1-oxide (1.23 g, 8.2 mmol) in methanol (20 ml) was heated in a sealed tube at 95° for 17 h. Evaporation of the solvent in vacuo gave a dark red oil which was chromatographed on silica gel (75 g). Elution with chloroform gave 2-cyano-3-methylpyrrole (102 mg, 11%), mp 70-72° (light petroleum) (lit.[18] mp 72°), also obtained in 68% yield by heating 2-cyano-1-hydroxy-3-methylpyrrole in MeOH at 95° for 18 h: ir (KBr) 3330 (NH) and 2205 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 9.50 (br s, 1 H, NH, exchanges with D_2O), 6.75 (d, 1 H, $J_{4,5}$ = 4 Hz, H_5), 5.91 (d, 1 H, $J_{4,5}$ = 4 Hz, H_4), and 2.09 (s, 3 H, 3-CH_3); *m/e* (rel abundance) 106 (57, $M\cdot^+$). Elution with chloroform-ether (1:1 v/v) gave 3-methoxy-3-methyl-2,3-dihydro-2-pyrrolone (492 mg, 48%), mp 60-63° (ether), identical with a sample kindly supplied by Dr. D. Lightner: ir (KBr) 3260 (NH) and 1700 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.79 (br s, 1 H, NH, exchanges with D_2O), 6.73 (d of d, 1 H, $J_{1,5}$ = 1 Hz; $J_{4,5}$ = 3.5 Hz, H_5), 6.48 (d of d, 1 H, $J_{1,4}$ = 0.5 Hz; $J_{4,5}$ = 3.5 Hz, H_4), 3.24 (s, 3 H, OCH_3), and 1.58 (s, 3 H, 3-CH_3); mass spectrum (70 eV) *m/e* (rel abundance) 127 (31, $M\cdot^+$), 112 (26), 99 (4), 96 (100, $M\cdot^+ - OCH_3$).

3-Methoxy-4-methyl-2,3-dihydro-2-pyrrolone (20d). This was similarly prepared from 2-azido-5-methylpyridine 1-oxide (872 mg, 5.8 mmol) in methanol (20 ml). Elution of the column with benzene gave 2-cyano-4-methylpyrrole (185 mg, 30%), bp 65° (0.08 mm) [lit.[18] bp 110° (0.2 mm)], also obtained in 65% yield by heating the *N*-hydroxypyrrole with methanol: ir (film) 3260 (NH) and 2205 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 9.85 (br s, 1 H, NH, exchanges with D_2O), 6.70 (d, 1 H, $J_{3,5}$ = 1.5 Hz, H_5), 6.60 (d, 1 H, $J_{3,5}$ = 1.5 Hz, H_3), and 2.06 (s, 3 H, 4-CH_3); *m/e* (rel abundance) 106 (9, $M\cdot^+$). Elution with chloroform-ether (1:1 v/v) gave 3-methoxy-4-methyl-2,3-dihydro-2-pyrrolone (330 mg, 45%): mp 74-76° (ether); ir (KBr) 3180 (NH) and 1670 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.99 (br s, 1 H, NH, exchanges with D_2O), 5.80 (d, 1 H, $J_{1,5}$ = 1 Hz, H_5), 5.20 (s, 1 H, H_3), 3.28 (s, 3 H, OCH_3), and 2.00 (s, 3 H, 4-CH_3); mass spectrum (70 eV) *m/e* (rel abundance) 127 [24, $M\cdot^+$], 96 (100, $M\cdot^+ - OCH_3$).

Anal. Calcd for $C_6H_9NO_2$: C, 56.69; H, 7.08. Found: C, 57.00; H, 7.32.

Thermolysis of 2-Azido-4,6-dimethylpyridine 1-Oxide in Methanol. A degassed solution of 2-azido-4,6-dimethylpyridine 1-oxide (4.50 g, 0.027 mol) in methanol (30 ml) was heated in a sealed tube at 90° for 20 h. Evaporation of the solvent in vacuo gave a residue which was chromatographed on silica gel (150 g). Elution with chloroform gave 2-cyano-3,5-dimethylpyrrole (2.18 g, 68%): mp 70-71° (lit.[18] mp 68-70°); ir (KBr) 3360 (NH) and 2225 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 9.10 (br s, 1 H, NH, exchanges with D_2O), 5.49 (s, 1 H, H_4), 2.14 (s, 3 H, CH_3), and 2.03 (s, 3 h, CH_3); mass spectrum (70 eV) *m/e* 120 (100, $M\cdot^+$).

4-Chloro-3-methoxy-2,3-dihydro-2-pyrrolone (20g). Decomposition of 2-azido-5-chloropyridine 1-oxide (1.00 g, 5.8 mmol) in methanol (20 ml) as above and elution of the column with benzene gave **4-chloro-2-cyanopyrrole** (42 mg, 6%): mp 71-73° (hexane); ir (KBr) 3260 (NH) and 2220 cm^{-1} (C≡N); NMR ($CDCl_3$) δ 10.33 (br s, 1 H, NH, exchanges with D_2O), 6.83 (d, 1 H, $J_{3,5}$ = 2 Hz, H_5), 6.72 (d, 1 H, $J_{3,5}$ = 2 Hz, H_3); *m/e* (rel abundance) 128 (26), 126 (100, $M\cdot^+$ ^{35}Cl).

Anal. Calcd for $C_5H_3ClN_2$: C, 47.46; H, 2.38. Found: C, 47.75; H, 2.68.

Elution with chloroform-ether (1:1 v/v) gave **4-chloro-3-methoxy-2,3-dihydro-2-pyrrolone** (256 mg, 28%), mp 96-98° (ethanol); ir (KBr) 3200 (NH) and 1730 cm^{-1} (C=O); NMR ($CDCl_3$) δ 7.20 (br s, 1 H, NH, exchanges with D_2O), 6.18 (d, 1 H, $J_{1,5}$ = 1 Hz, H_5), 5.40 (s, 1 H, H_3), and 3.28 (s, 3 H, OCH_3); *m/e* (rel abundance) 149 (1.5), 147 (4, $M\cdot^+$), 118 (33), 116 (100, $M\cdot^+ - OCH_3$).

Anal. Calcd for $C_5H_6ClNO_2$: C, 40.68; H, 4.07. Found: C, 41.00; H, 4.42.

Thermolysis of 2-Azidopyridine 1-Oxide (3a) in Aniline. A degassed solution of 2-azidopyridine 1-oxide (2.00 g, 0.016 mol) in aniline (20 ml) was heated in a sealed tube at 95° for 12 h. Evaporation of the solvent in vacuo gave a residue which was chromatographed on silica gel. Elution with benzene gave 2-cyanopyrrole (390 mg, 22%), bp 85-88° (0.1 mm), identical with an authentic sample.

Elution with chloroform-ether (1:1 v/v) gave **3-anilino-2,3-dihydro-2-pyrrolone *N*-phenylimine (22a)** (1.11 g, 26%): mp 137-139° (95% ethanol).

Anal. Calcd for $C_{16}H_{15}N_3$: C, 77.11; H, 6.02. Found: C, 77.16; H, 6.09.

Elution with chloroform-ethanol (1:1 v/v) gave 2-aminopyridine 1-oxide (426 mg, 24%), mp 158-159°, identical with an authentic sample.

A solution of 3-anilino-2,3-dihydro-2-pyrrolone-*N*-phenylimine (100 mg, 4 mmol) in aqueous 5% KOH (20 ml) was stirred at 40° overnight. Acidification with dilute HCl, extraction with $CHCl_3$, and evaporation of the solvent gave 3-anilino-2,3-dihydro-2-pyrrolone (43 mg, 58%): mp 89-90° dec (water); ir (KBr) 3300, 3180, 1690, 1620, 1600, 1485, 1420, 1273, 1182, 941, 820, and 770 cm^{-1}; NMR ($CDCl_3$) δ 7.93 (br s, 1 H, NH, exchangeable), 7.85-6.21 (m, 7 H, phenyl H, H_4 and H_5), 5.27 (s, 1 H, H_3), and 3.98 (br s, 1 H, NH, exchangeable); mass spectrum (70 eV) *m/e* (rel abundance) 175 (16, $M\cdot^+$ + 1), 174 (23, $M\cdot^+$), 121 (47), 119 (61), 117 (43), 108 (36), (100), 77 (82), 66 (39).

Thermolysis of 2-Azido-4-methylpyridine 1-Oxide (3c) in Aniline. A solution of 2-azido-4-methylpyridine 1-oxide (850 mg, 5.7 mmol) in aniline (20 ml) was heated in a sealed tube at 100° for 4 hr. Evaporation of the solvent in vacuo gave a residue which was chromatographed on silica gel. Elution with chloroform gave 2-cyano-3-methylpyrrole (95 mg, 16%): mp 70-72° (lit.[18] mp 72°).

Further elution with chloroform gave **3-anilino-3-methyl-2,3-dihydro-2-pyrrolone** (525 mg, 49%): mp 173-174° (EtOH); ir (KBr) 3300, 3030, 2920, 1690, 1596, 1521, 1500, 1316, 1248, 1126, 1080, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 7.80 (br s, 1 H, NH, exchangeable), 7.37 (m, 5 H, phenyl H), 6.75 (d of d, 1 H, $J_{1,5}$ = 1 Hz; $J_{4,5}$ = 4 Hz, H_5), 6.46 (d of d, 1 H, $J_{1,4}$ = 0.5 Hz; $J_{4,5}$ = 4 Hz, H_4), 3.95 (br s, 1 H, NH, exchangeable), and 1.85 (s, 3 H, 3-CH_3); *m/e* 188 ($M\cdot^+$).

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.42. Found: C, 70.28; H, 6.55.

Thermolysis of 2-Azido-5-methylpyridine 1-Oxide (3d) in Aniline. A similar decomposition of 2-azido-5-methylpyridine 1-oxide (1.50 g, 0.01 mol) in aniline (25 ml) gave 2-cyano-4-methylpyrrole (251 mg, 24%), bp 71° (0.09 mm) (lit.[18] bp 110° (0.2 mm)) and **3-anilino-4-methyl-2,3-dihydro-2-pyrrolone** (1.05 g, 55%): mp 145-147° (EtOH); ir (KBr) 3310, 3190, 3030, 2910, 1690, 1595, 1516, 1500, 1315, 1250, 1220, 1125, 1080, and 750 cm^{-1}; NMR ($CDCl_3$) δ 7.86 (br s, 1 H, NH, exchangeable), 7.41 (m, 5 H, phenyl H), 5.74 (d, 1 H, $J_{1,5}$ = 1 Hz, H_5), 5.12 (s, 1 H, H_3), 4.20 (br s, 1 H, NH, exchangeable), and 2.15 (s, 3 H, 4-CH_3); mass spectrum (70 eV) *m/e* 188 ($M\cdot^+$).

Anal. Calcd for $C_{11}H_{12}N_2O$: C, 70.19; H, 6.42. Found: C, 70.17; H, 6.47.

Thermolysis of 2-Azido-5-chloropyridine 1-Oxide (3g) in Aniline. Decomposition of 2-azido-5-chloropyridine 1-oxide (1.87 g, 0.011 mol) in aniline (50 ml) gave 4-chloro-2-cyanopyrrole (63 mg, 5%): mp 70-72° (hexane), identical with the sample obtained above, and **3,4-dianilino-2,3-dihydro-2-pyrrolone *N*-phenylimine** (1.17 g, 31%): mp 173-174° (EtOH); ir (KBr) 3320, 3165, 1660, 1620, 1600, 1485, 1408, 1280, 1195, and 750 cm^{-1}; NMR ($CDCl_3$) δ 7.83 (br s, 1 H, NH, exchangeable), 7.52-7.36 (m, 5 H, phenyl H), 7.25-7.10 (m, 5 H, phenyl H), 6.95-6.82 (m, 5 H, phenyl H), 6.19 (d, 1 H, $J_{1,5}$ = 1 Hz, H_5), 6.10 (s, 1 H, H_3), and 4.60-3.80 (br s, 2 H, NH, exchangeable); mass spectrum (70 eV) *m/e* 340 ($M\cdot^+$).

Anal. Calcd for $C_{22}H_{20}N_4$: C, 77.65; H, 5.89. Found: C, 77.65; H, 5.85.

Elution with chloroform-ethanol (1:1 v/v) gave 2-amino-5-chloropyridine 1-oxide (623 mg, 45%), mp 189-191° (EtOH) (lit.[34] mp 191-193°), identical with an authentic sample.

Thermolysis of 3g in Morpholine. A degassed solution of **3g** (2.80 g) in morpholine (35 ml) was heated in a Fischer-Porter tube at 100° for 12 h. Evaporation of the solvent in vacuo gave a dark-red oil (2.10 g) which was chromatographed on silica gel (150 g). Elution with benzene gave **5-chloro-2-*N*-morpholinopyridine** (550 mg, 11%), identical with an authentic sample prepared as below. Elution with $CHCl_3$ gave **4-chloro-3-*N*-morpholino-2,3-dihydro-2-pyrrolone** (368 mg, 11%): mp 137-139° (hexane); ir (KBr) 3200 (NH), 1675 (C=O), and 1625 cm^{-1} (C=C); NMR ($CDCl_3$) δ 7.35 (br s, 1 H, NH, exchangeable), 6.15 (d, 1 H, $J_{1,5}$ = 1 Hz, H_5), 5.26 (s, 1 H, H_3), and 3.67 (m, 8 H, morpholine protons); *m/e* (rel abundance) 204 (8), 203 (6), 202 (27, $M\cdot^+$ ^{35}Cl), 114 (100).

Anal. Calcd for $C_8H_{11}ClN_2O_2$: C, 47.4; H, 5.43. Found: C, 47.30; H, 5.28.

Elution with $CHCl_3EtOH$ (1:1 v/v) gave 2-amino-5-chloropyridine 1-oxide (1.14 g, 48%), identical with an authentic sample.

5-Chloro-2-*N*-morpholinopyridine. A solution of 2,5-dichloropyridine (100 g) in morpholine (15 ml) was heated at 100° for 3 h. Morpholine hydrochloride (315 mg, 38%), mp 175–176°, separated and was filtered. Unreacted 2,5-dichloropyridine (400 mg, 40%), mp 56–58°, was sublimed out of the residue remaining after evaporation of the solvent. The residual oil was distilled in vacuo to give the **product** (425 mg, 53%): bp 161–163° (0.1 mm); ir (film) 3100 cm^{-1} (NH); NMR (CCl_4) δ 8.10 (d 1 H, $J_{4,6}$ = 3 Hz, H_6), 7.35 (d of d, 1 H, $J_{3,4}$ = 9 Hz, $J_{4,6}$ = 3 Hz, H_4), 6.43 (d, 1 H, $J_{3,4}$ = 9 Hz, H_3), and 3.50 (m, 8 H, morpholine protons); *m/e* rel abundance) 200 (24), 199 (3), 198 (87, $M\cdot^+$ ^{35}Cl), 163 (6, $M\cdot^+$ − Cl), 112 (100).

Anal. Calcd for $C_9H_{11}ClN_2O$: C, 54.41; H, 5.54. Found: C, 54.87; H, 5.86.

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