Synthetic Applications of *N*–*N* Linked Heterocycles. Part 4.[1] The Reaction between 1-Pyridinio-4-pyridone Cations and Cyanide Ion: Mechanism of Cyanopyridine Formation, and a Regioselective Synthesis of 4-Cyanopyridines

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The 1-pyridinio-4-pyridone cations (1) give with aqueous sodium cyanide mixtures of 2- and 4-cyanopyridines, 2-cyanopyridine formation being favoured by high cyanide ion concentration, and 4-cyanopyridine formation by low cyanide ion concentration, when small amounts of the intermediate 1,4-dihydro-4-cyano-adducts (7) or (9) are also observed. The 2,6-dimethyl-1-pyridinio-4-pyridone cations (2) in contrast give high yields of the 1,4-dihydro-4-cyano-adducts (8) or (10), the former being decomposed quantitatively by heat to 4-cyanopyridines and 2,6-dimethyl-4-pyridone. Only very small amounts of 2-cyanopyridines are formed. Mechanisms for the two reactions are proposed which account for the experimental observations.

SINCE the independent discoveries by Feely and Beavers [2] and Okamoto and Tani [3] that cyanopyridines can be prepared by the action of aqueous potassium cyanide on *N*-alkoxypyridinium salts, the reaction has been used in the synthesis of a large number of derivatives.[4] Although both 2- and 4-cyano-derivatives are formed, the 2-cyano-product generally predominates at room temperature. In contrast, Okamoto and his co-workers [5] showed that 1-(*N*-acylalkylamino)pyridinium salts (13) gave with potassium cyanide high yields of 4-cyanopyridines, with only small amounts of the 2-isomers.

Recently we reported that the pyridiniopyridone (1a) with saturated aqueous potassium cyanide gave 2-cyanopyridine (3a) in 87% yield, together with a negligible amount of the 4-isomer (4a).[6] In an attempt to rationalise the differences in behaviour shown by the three types of pyridinium salts we have studied the reactions of a variety of substituted pyridiniopyridones (1), (2) with cyanide ion at different concentrations, and carried out additional experiments to establish whether the mechanism is analogous to that proposed by the other groups.[2,3a,5a]

RESULTS

Aqueous solutions of sodium cyanide of different concentrations were added at room temperature to solutions of fixed concentration of pyridiniopyridones (1) and (2), and the products extracted into chloroform and examined by ^{1}H n.m.r. spectroscopy. The results are presented in Tables 1 and 2, and the following observations can be made.

Pyridiniopyridones (1).—Both 2- and 4-cyanopyridines were formed unless appropriately sited alkyl groups prevented this [*e.g.* (1d) and (1f)]. However 2-cyanopyridine (3) formation was favoured by high CN^- concentration and 4-cyanopyridine (4) by low CN^- concentration,

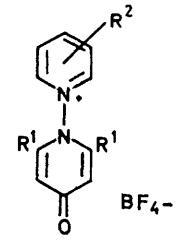
TABLE 1

Reactions of aqueous NaCN with pyridiniopyridones (1)

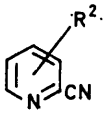
Compound	Concn. (1) [a] (mol dm^{-3})	Concn. CN^- [a] (mol dm^{-3})	Ratio [a] CN^- : (1)	Yield (%) (3)	(4)	Other	Total	Ratio 2-attack : 4-attack
(1a)	0.314	2.74	8.73	37	17		54	2.2
	0.312	1.36	4.36	34	23		57	1.5
	0.314	0.776	2.47	7	51		58	0.14
	0.317	0.343	1.08	[b]	[b]	9 [c]	9	
(1b)	0.298	2.84	9.53	30	13		43	2.3
	0.295	1.33	4.51	29	14		43	2.1
	0.301	0.686	2.28	10	12		22	0.83
	0.299	0.335	1.12	[b]	17		17	
(1c)	0.309	3.07	9.94	40	13	7 [d]	60	3.7
	0.326	1.48	4.54	34	18	7 [d]	59	2.3
	0.312	0.939	3.01	25	32	6 [d]	63	1.0
	0.318	0.379	1.19	6	60	2 [d]	68	0.13
(1d)	0.333	3.09	9.28	42		6 [e]	52	7.0
	0.326	1.50	4.60	35		11 [e]	46	3.2
	0.324	0.775	2.39	23		9 [e] 4 [f]	36	3.0
	0.321	0.392	1.22	5		7 [e] 4 [f]	16	1.2
(1f)	0.280	2.89	10.32		81		81	
	0.279	1.43	5.12		77		77	
	0.279	0.726	2.60		74		74	
	0.279	0.371	1.33		33		33	
(1e) [g]	0.295	1.39	4.71	33		18 [h]	51	1.8
(1g) [g]	0.200	2.40	12.00			38 [i]	38	

[a] Initial value, on mixing. [b] Too small to measure. [c] Compound (7a), isolated yield; half-life *ca.* 2 h as 5% solution in $CDCl_3$ at 34 °C. [d] 2-Cyano-5-methylpyridine. [e] Compound (9a), isolated yield. [f] Ring-opened material (17). [g] Effect of CN^- concentration not studied. [h] Compound (9b). [i] Compound (9f).

and total yields of cyanopyridines decreased sharply when the mole ratio of CN^- to pyridiniopyridone (1) fell below 2. In certain cases, the 1,4-dihydropyridine derivatives (7) or (9) could be isolated, and compound (9f) was the only



(1) R^1 = H
(2) R^1 = Me



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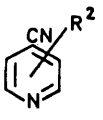

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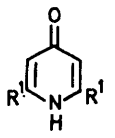

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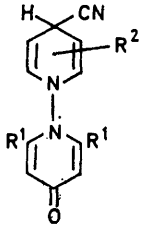

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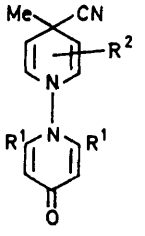
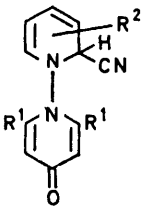


(9) R^1 = H
(10) R^1 = Me



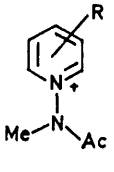
(11) R^1 = H
(12) R^1 = Me

R^2

a; H
b; 2-Me
c; 3-Me
d; 4-Me

R^2

e; 2,4-Me_2
f; 2,6-Me_2
g; 2,4,6-Me_3
h; 2-Me, 5-Et



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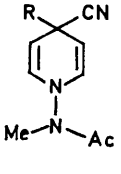
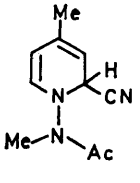


(14) a; R = H
b; R = Me



(15)

product observed from the pyridiniopyridone (1g). Derivatives of type (7) however decomposed spontaneously and quantitatively in the n.m.r. tube ($CDCl_3$ solution) to 4-cyanopyridines (4) and pyridone (5) within a few hours. In one case, (1d), a ring-opened compound (17) was isolated as a by-product, derived apparently from the 1,2-dihydro-intermediate (11d).

Pyridiniopyridones (2) —Here also the yield of products dropped significantly when the mole ratio of CN^- to pyridiniopyridone fell below 2. However, the major (and often the only) product was the 1,4-dihydro-derivative (8) or (10), cyanopyridines (3) and (4) being mostly undetectable by ^1H n.m.r. spectroscopy.* Derivatives (8) were very much more stable than the analogous compounds (7), as shown by their half-lives in $CDCl_3$ solution at room temperature (Table 2). Nevertheless, they decomposed rapidly and quantitatively on heating to 4-cyanopyridines (4) and pyridone (6).

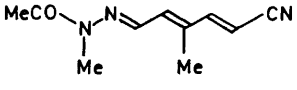
TABLE 2

Reaction of aqueous NaCN with pyridiniopyridones (2)

Compound	Concn. (2) (mol dm^{-3})	Concn. CN^- (mol dm^{-3})	Ratio CN^- : (2)	Yield % (9); (*10*)	Half life (h) [a]
(2a)	0.275	3.14	11.42	78	73
	0.272	1.37	5.04	77	
	0.266	0.555	2.09	78	
	0.264	0.298	1.13	*b*	
(2b)	0.283	3.10	10.95	60	55
	0.283	1.50	5.30	64	
	0.286	0.731	2.56	72	
	0.283	0.335	1.18	37	
(2c)	0.272	3.20	11.76	82	75
	0.274	1.51	5.51	83	
	0.270	0.628	2.34	74	
	0.269	0.326	1.21	88	
(2d)	0.285	3.00	10.52	*79*	*c*
	0.283	1.43	5.05	*76*	
	0.281	0.731	2.60	*64*	
	0.281	0.351	1.25	*39*	
(2e)	0.256	2.76	10.78	*67*	*c*
	0.267	1.43	5.36	*51*	
	0.271	0.702	2.59	*20*	
	0.256	0.384	1.50	*1.2*	
(2h)	0.266	2.74	10.30	99	14
	0.259	1.46	5.64	99	
	0.255	0.799	3.13	69	
	0.255	0.416	1.63	59	

[a] Measured as 5% $CDCl_3$ solution by ^1H n.m.r. at 34 °C. [b] Too small to measure. [c] Stable compounds.

To determine whether 1,4-dihydropyridine formation was reversible, derivatives (7a) and (10a) were stirred at room temperature with an excess of aqueous sodium cyanide. Compound (7a) gave a mixture of cyanopyridines (3a) and (4a) [ratio 1 : 1], and compound (10a) a quantitative yield of the 2-cyanopyridine (3d). When the experiment was



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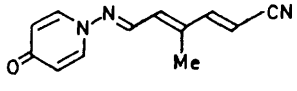

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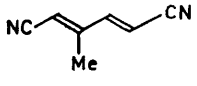

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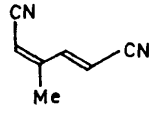


(19)

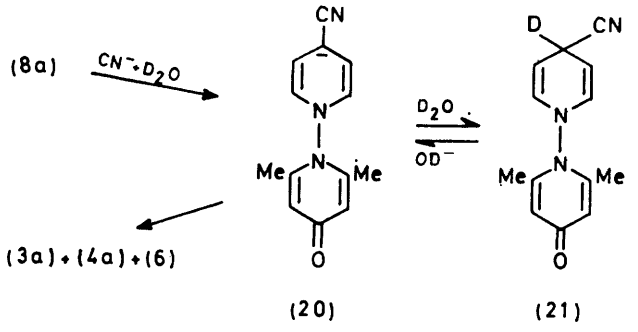
repeated with a mixture of adduct (9a) and ring-opened compound (17), the 2-cyanopyridine (3d) was produced together with a mixture of dicyanobutadienes (18) and (19),† formed by elimination of the pyridone (5) from compound (17).

* When cyanopyridines were detected, the total yield was less than 5%, and the 4-cyano-product predominated.

† Assigned from ^1H n.m.r. spectra. Both isomers contain a *trans* disubstituted double-bond (*J* 16 Hz), and one (18) has a spectrum identical with that of one of two isomers reported previously.[7] The configuration of the second double bond is assigned from the coupling constant of the methyl doublet [2.5 Hz for (18) and 1.4 Hz for (19)].

Intermediate (8a) was stirred with sodium cyanide in D_2O solution, to establish whether elimination to products (4a) and (6) was concerted, or went *via* a carbanionic intermediate (20) (Scheme 1). After 18 h, the product comprised starting material (8a) and cyanopyridines (3a) and (4a) [ratio 3 : 2 : 15 respectively]. There was no evidence for deuterium-exchanged product (21) either by ^1H n.m.r. or by i.r. spectroscopy.

Spectra of 1,4-Dihydropyridines (7)—(10).—^1H N.m.r., i.r., u.v., and mass spectral data are displayed in Table 3. Only one peak was observed in the u.v. region, characteristic of the pyridone chromophore.[8] The ^1H n.m.r. spectra showed absorption in the range 4—6 p.p.m. characteristic of the dihydropyridine ring protons, and in the cases of compounds (8) and (10) separate signals for the 2- and 6-methyl groups, indicating restricted rotation about the N–N bond. Mass spectra all showed a parent peak (1—10%), and while N–N bond-cleavage was the major process giving pyridones (5) or (6) and cyanopyridine fragments, loss of HCN by compounds (9) and (10) to give $M - 27$ fragments was also important (>50%).



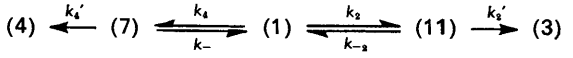
SCHEME 1

DISCUSSION

Pyridiniopyridones (1).—The results obtained from the reaction with cyanide ion are fully consistent with a mechanism proceeding *via* dihydro-intermediates (7) and (11) as shown in Scheme 2, and in this respect are analogous to results obtained with other leaving groups on the pyridinium nitrogen atom.[2,3a,5a] Though no 1,2-dihydro-derivatives (11) were observed directly, the isolation of ring-opened material (17) together with cyanopyridine (3d) from pyridiniopyridone (1d) is taken as strong evidence for the intermediacy of compound (11d).* The isolation of 1,4-dihydro-derivative (7a) and the observed spontaneous decomposition of derivatives (7a), (7b), and (7c) in $CDCl_3$ solution to the corresponding 4-cyanopyridines (4) and pyridone (5) essentially confirms the intermediacy of compounds (7) in the formation of 4-cyanopyridines. Okamoto [5a] isolated a 1,4-dihydro-intermediate (14a) which decomposed quantitatively to 4-cyanopyridine (4a), but in contrast to this work did not observe analogues of the 4-methyl compounds (9) [*e.g.* compound (14b)], nor did he observe any reaction between cyanide ion and the 2,4,6-trimethylpyridinium salt (13; R = 2,4,6-Me_3).

The reversible formation of intermediates (7) and (11) from pyridiniopyridone (1) is confirmed by the conversion of compound (7a) into a mixture of cyanopyridines (3a) and (4a) on stirring with aqueous sodium cyanide, and is further supported by the analogous conversion of the 4-methyl intermediates (9a) and (10a) into the 2-cyanopyridine (3d).

An explanation is needed to account for the increase in the ratio of products (4) : (3) as the CN^- concentration falls.† The effect of concentration of CN^- on its reactions with *N*-alkoxypyridinium salts does not appear to have been studied, but a similar change in orientation of attack was observed by Okamoto and his co-workers as a function of CN^- concentration in the reaction with 3-substituted pyridinium salts (13; R = 3-Br, or 3-MeO).[9] To account for this, he suggested a mechanism analogous to that shown in Scheme 2, with the restrictions that addition of CN^- was irreversible (k_{-2}, $k_{-4} \approx 0$), the elimination steps were rate-controlling, and $k_4 > k_2$ but $k_{2'} > k_{4'}$.



SCHEME 2

Since we have established the reversibility of CN^- addition to the salts (1), our data are better accommodated by the requirement that $k_2 > k_4$ [attack at the 2-position is kinetically controlled] and that $k_{-4} < k_{-2}$ [intermediates (7) are thermodynamically more stable than intermediates (11)]. At high CN^- concentration, fragmentation of the rapidly formed intermediate (11) to 2-cyanopyridine will be fast, leading to relatively high yields of products (3). At lower CN^- concentration, the rate of fragmentation of intermediate (11) may become less than the rate of conversion (11)→(1),‡ allowing the equilibrium (7)⇌(1)⇌(11) to become established. Thus the concentration of intermediate (7) would increase relative to (11) and consequently so would the product ratio (4) : (3). The isolation of intermediate (7a) and the observation of (7b) and (7c) at low CN^- concentration implies that the fragmentation step is rate-limiting in the sequence (1)→(7)→(4); if the above argument is valid, fragmentation would also have to be rate-limiting in the sequence (1)→(11)→(3). A similar argument would account for Okamoto's results if the

* Okamoto [9] claimed to have isolated a 1,2-dihydro-derivative (15), but a comparison of the published ^1H n.m.r. and u.v. data with ours for compound (17) shows that it is almost certainly the ring-opened isomer (16). Curiously, both in our work and in Okamoto's, ring-opening was observed only in the case of the 4-methylpyridinium salt. [In this work, compound (1d) but not compound (2d).]

† In this work, isomer ratios were calculated from accurate integrals of the ^1H n.m.r. spectra of crude reaction mixtures (which, however, contained only cyanopyridines and 1,4-dihydro-intermediates). They are thus quite reliable. Yields, however, are isolated yields, and may be in error by as much as 10—20%

‡ It seems reasonable to assume that the rates of fragmentation of intermediates (7) and (11) will depend on the concentration of base present in solution (either as CN^- or as derived OH^-), whereas their rates of decomposition back to (1) should be independent of CN^- concentration.

reversibility of CN^- addition to the salts (13) could be established.

Pyridiniopyridones (2).—The reaction between CN^- and pyridiniopyridones (1) neither gives attractive yields of cyanopyridines, nor is it usefully regioselective. In contrast, the reaction with pyridiniopyridones (2) is highly regioselective, attack of CN^- occurring almost exclusively at the 4-position of the pyridinium ring, giving high yields of intermediates (8) which may be converted essentially quantitatively into 4-cyanopyridines (4). There is no significant increase in attack at the 2-position even when the 4-position of the pyridinium ring is blocked by a methyl group, high yields of stable intermediates (10) being isolated. The results can be explained by a reaction scheme analogous to Scheme 2, but with the requirement that $k_4 \gg k_2$ to accommodate the regioselectivity, and $k_{4'}$ [(8)→(4)] < $k_{4'}$ [(7)→(4)] to accommodate the greater stability of intermediates (8) over intermediates (7). This difference in stability is presumably related to different configurations in the transition states leading to 4-cyanopyridines and pyridone, since the experiment in D_2O indicates that the elimination is concerted.

Previous workers have found with analogous reactions that the ratio of products (4) : (3) is increased by having a bulky group attached to the pyridinium nitrogen atom.[2,3b,5a] A molecular model of compound (2a) shows that steric factors require the planes of the two rings to be at right angles,* and that the resulting positions of the two methyl groups should hinder approach of nucleophiles at the 2- and 6-positions of the pyridinium ring. Since reactions of compounds (1) and (2) with cyanide ion were carried out under identical sets of conditions, the steric effect of the methyl groups appears to account for the regioselectivity in the latter.

Thus pyridiniopyridones (2) suggest themselves as potential intermediates for the synthesis of other 4-substituted pyridines *via* attack with suitable nucleophiles.

* The torsion angle between the two rings has been found to be 90° by *X*-ray crystallography.[10] The non-coplanarity of the two rings in (2) has been indicated by u.v. spectroscopy;[6] and is further confirmed by the non-equivalence (^1H n.m.r.) of the methyl groups in the pyridone ring of compounds (8) and (10), showing lack of free rotation about the N–N bond.

EXPERIMENTAL

1-Pyridinio-4-pyridones (1) *and* (2).—Compounds (1a—d) and (2a—d, h) were prepared by reported procedures.[6] The dimethyl derivatives (1e) and (2e) were prepared analogously from 1-amino-2,4-dimethylpyridinium chloride and respectively chelidonic acid or dehydroacetic acid; yield *tetrafluoroborate* (1e) (80%), prisms from EtOH, m.p. 163—165 °C (Found: C, 41.8; H, 4.0; N, 7.9. $(C_{12}H_{13}BF_4N_2O)_2{\cdot}HBF_4{\cdot}H_2O$ requires C, 42.2; H, 3.8; N, 8.2%); yield *tetrafluoroborate* (2e) (40%), prisms from EtOH, m.p. 193—195 °C (Found: C, 41.0; H, 5.3; N, 6.7. $(C_{14}H_{17}BF_4N_2O)_2{\cdot}HBF_4{\cdot}3H_2O$ requires C, 41.5; H, 5.55; N, 6.9). The derivatives (1f) and (1g) were prepared from the appropriate 1-aminopyridinium chloride and 4-pyrone; yield *tetrafluoroborate* (1f) (88%), prisms from EtOH, m.p. 180—182 °C [Found: C, 43.4; H, 4.4; N, 8.45. $(C_{12}H_{13}BF_4N_2O)_2{\cdot}HBF_4{\cdot}H_2O$ requires C, 43.45; H, 4.4; N, 8.45%]; yield tetrafluoroborate (1g) (81%), plates from EtOH, m.p. 136—140 °C (Found: C, 44.7; H, 4.7; N, 8.0. $(C_{13}H_{15}BF_4N_2O)_2{\cdot}HBF_4$ requires C, 45.1; H, 4.5; N, 8.1%).

TABLE 3

Spectroscopic data for compounds (7), (8), (9), and (10)

Compound	δ [a] 2,6	3,5	2'	3'	4'	5'	6'	$\nu_{max.}$/cm^{-1} [b] principal common bands				$\lambda_{max.}$/nm [c] [log ε]	$M^{+\cdot}$ (%) [d]
(7a)	7.40	6.33	6.24	4.94	4.25	4.94	6.24	2 232	1 681	1 634	1 574	262.5 [4.24]	199 (5.0)
(7b)	7.39	6.35	*1.67*	4.75	4.25	4.94	6.21			[e]		*e*	*e*
(9a)	7.38	6.34	6.18	4.91	*1.60*	4.91	6.18	2 221	1 680	1 635	1 580	263.5 [4.33]	213 (38.5)
(9b)	7.33	6.35	*1.69*	4.77	*1.58*	4.96	6.22	2 220		1 633	1 565	260.5 *f*	227 (0.7)
(9g)	7.37	6.36	*1.68*	4.79	*1.54*	4.79	*1.68*	2 228	1 695	1 622	1 574	263.5 [4.34]	241 (13.0)
(8a)	*2.22* *2.32*	6.09	6.13	4.78	4.30	4.78	6.13	2 230	1 682	1 648	1 570	261.5 [4.29]	227 (0.4)
(8b)	*2.20* *2.30*	6.14	*1.60*	4.55	4.28	4.71	6.10	2 226	1 680	1 644	1 580	260.0 [4.32]	241 (1.8)
(8c)	*2.18* *2.28*	6.08	5.93	*1.83*	4.15	4.73	6.14	2 230	1 693	1 647	1 572	261.5 [4.30]	241 (0.2)
(8h)	*2.19* *2.29*	6.15	*1.59*	4.58	4.22	*1.11* *2.19*	5.89	2 230	1 694	1 630	1 578	262.5 [4.34]	269 (0.6)
(10a)	*2.20* *2.29*	6.07	6.08	4.75	*1.59*	4.75	6.08	2 228	1 679	1 648	1 568	262.0 [4.32]	241 (3.5)
(10b)	*2.17* *2.26*	6.12	*1.58*	4.58	*1.55*	4.77	6.09	2 221	1 682	1 634	1 560	263.0 [4.37]	255 (1.5)

[a] In $CDCl_3$ on Perkin-Elmer R–20 spectrometer. Primed substituents positions refer to the dihydropyridine ring. Values in italics are for alkyl substituents. [b] Recorded on a Perkin–Elmer 577 instrument in Nujol. [c] Recorded on Beckman Acta CIII in ethanol. [d] Recorded on Hitachi RMS–4. [e] Too unstable to isolate. [f] Insufficiently pure to obtain log ε.

Reaction of the Pyridiniopyridones (1) *and* (2) *with Sodium Cyanide.*—A general procedure is described; results are summarized in Tables 1 and 2. To a stirred solution of the appropriate pyridiniopyridone tetrafluoroborate (4 ml; *ca.* 0.3M) was added a solution of sodium cyanide of the selected concentration (1 ml) all at once. An immediate yellow or red colour was observed, and in many cases the product was precipitated from solution in 2—3 min. After being

stirred for 15 min, the mixture was extracted with $CHCl_3$ (3 × 15 ml), swirled with a little charcoal (if necessary), and dried ($MgSO_4$). Removal of the solvent at room temperature under reduced pressure in a tared flask gave the crude product, which was taken up in $CDCl_3$ and examined by ^1H n.m.r. spectroscopy.

Isolation of the adducts (7), (8), (9), *and* (10). Crude products from removal of $CHCl_3$ (above) were dissolved in $CHCl_3$ (5 ml), and light petroleum (b.p. 40—60 °C) was added dropwise with stirring until precipitation was complete. After two further recrystallisations products were analysed by i.r., u.v., ^1H n.m.r., and mass spectroscopy. Results are given in Table 3. Adducts (9) and (10) were stable enough to be submitted for microanalysis, but some were found to contain residual water which could not be removed without decomposition of the adduct. *Adduct* (9a), m.p. 149—149.5 °C (Found: C, 65.7; H, 5.3; N, 18.6. $C_{12}H_{11}N_3O\cdot\frac{1}{3}H_2O$ requires C, 65.7; H, 5.35; N, 19.15%); *adduct* (9g), m.p. 118—120 °C (Found: C, 69.3; H, 6.2; N, 17.05. $C_{14}H_{15}N_3O$ requires C, 69.7; H, 6.3; N, 17.4%); *adduct* (10a) (Found: C, 65.3; H, 6.3; N, 16.0. $C_{14}H_{15}N_3O\cdot H_2O$ requires C, 64.85; H, 6.6; N, 16.2%); *adduct* (10b) (Found: C, 70.3; H, 6.5; N, 16.1. $C_{15}H_{17}N_3O$ requires C, 70.6; H, 6.7; N, 16.45%).

Identification of the cyanopyridines (3) *and* (4). 4-Cyanopyridines (4) were obtained by pyrolysis of the appropriate adduct (8) [60 °C; 1 Torr], the product being collected on a cold-finger condenser, and its m.p. and ^1H n.m.r. spectrum recorded; the latter to assist in the analysis of crude products above. Product (4f) was obtained directly from pyridiniopyridone (1f) and sodium cyanide. 4-Cyanopyridines are given together with recorded m.p. and literature m.p. respectively: (4a), 79—80 °C, 80—82 °C;[2] (4b), 44—45 °C, 45—46.5 °C;[3a] (4c), 49—50 °C, 51 °C;[3a] (4f), 79—80 °C, 77—81 °C.[2]

2-Cyanopyridine (3a) was identified by comparison of its ^1H n.m.r. spectrum with that of an authentic sample. Compounds (3d) and (3e) were obtained from the mother liquors from the recrystallisation of adducts (9a) and (9b), and purified by sublimation. Compounds (3b) and (3c) were separated from the 4-isomers by chromatography on alumina, with benzene–light petroleum (1 : 9) as eluant. ^1H N.m.r. spectra were recorded, and m.p.s together with literature values for each follow: (3b), 70—71 °C, 72—74 °C;[2] (3c), 88—89 °C, 87—90 °C;[2] (3d), 88—89 °C, 89 °C;[3a] (3e), 53—54 °C, 55—56 °C.[2]

Isolation of the ring-opened compound (17). The crude product from the reaction between compound (1d) and sodium cyanide (mol ratio 1 : 2.5) was triturated with Et_2O to remove the cyanopyridine (3d), and then with CH_2Cl_2 to extract the dihydro-adduct (9a). Recrystallisation of the residue from methanol gave ring-opened compound (17) too unstable for microanalysis, m.p. 146—147 °C; $M^{+\cdot}$ 213; $\nu_{max.}$ 2 226, 1 639, 1 584, 1 165, and 1 130 cm^{-1}; $\lambda_{max.}$ 263 (log ε 4.23) and 344 nm (4.34); δ[$(CD_3)_2SO$] 9.08 (1 H, d, *J* 9.8 Hz), 8.31 (2 H, d, *J* 8.3 Hz), 8.29 (1 H, d, *J* 16.5 Hz), 6.56 (1 H, dm, *J* 9.8 Hz), 6.32 (2 H, d, *J* 8.3 Hz), 6.06 (1 H, d, *J* 16.5 Hz), and 2.15 (3 H, m, $J \sim 1.2$ Hz).

Reaction of the Adducts (7a), (9a), *and* (10a) *with Sodium Cyanide*.—Solutions of NaCN (3×10^{-3} mol) in water (1 ml) and of adduct (7a) (1×10^{-4} mol) in water (2 ml) were mixed and stirred at room temperature for 3 h. Extraction with $CHCl_3$, drying of the extract ($MgSO_4$), and evaporation of the solvent gave a mixture of cyanopyridines (3a) and (4a) [ratio 1 : 1; identified by ^1H n.m.r. spectroscopy]. Similarly, adduct (10a) gave, in 8 h, the 2-cyanopyridine (3d). A mixture of compounds (9a) and (17) [4.3×10^{-4} mol; ratio 1 : 1] and NaCN (2.75×10^{-3} mol) in water (3 ml) after 12 h gave likewise the 2-cyanopyridine (3d) and a mixture of dicyanobutadienes (18), δ($CDCl_3$) 7.03 (1 H, d, *J* 16 Hz), 5.71 (1 H, d, *J* 16 Hz), 5.57 (1 H, m), and 2.18 (3 H, d, *J* 2.5 Hz); and (19), δ($CDCl_3$) 7.60 (1 H, d, *J* 16 Hz), 5.75 (1 H, d, *J* 16 Hz), 5.54 (1 H, m), and 2.07 (3 H, d, *J* 1.4 Hz), as an oil which was not separated into its components.

Attempted Deuterium Exchange with the Adduct (8a).—The pyridiniopyridone (2a) (2.0×10^{-3} mol) was added to a solution of NaCN (2.0×10^{-2} mol) in D_2O (8 ml) and the mixture stirred for 1 min to form the adduct (8a). Dichloromethane (16 ml) was added, and the mixture stirred vigorously at room temperature for 18 h. The CH_2Cl_2 layer was separated, dried ($MgSO_4$), evaporated, and the residue examined by i.r. and ^1H n.m.r. spectroscopy ($CDCl_3$).

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