N-Oxides and Related Compounds. Part 55.[1] 1-Pyridinio-4-pyridone Cations and 1-Pyridiniopyridinium Dications: Preparation and Reactions[2]

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1-Aminopyridinium cations react with 4-pyrone and various derivatives to give 1-pyridinio-4-pyridones [(4) and (5)], which are converted by phosphoryl chloride into 4-chloropyridiniopyridinium salts [(6) and (7)]. These compounds are transformed into 1-arylpyridinium salts, pyridine disulphones, cyanopyridines, and aminopyridiniopyridinium cations in reactions of potential synthetic utility.

CONVERSION of a nitrogen heteroaromatic compound into its *N*-oxide is of great synthetic importance;[3] however, despite increasing interest,[4] the chemistry of *N*-aminoheterocycles remains unexploited. We believe *NN*-linked biheteroaryls to be of synthetic potential, and have recently described synthetic methods[5] which, however, failed for 1,1'-bipyridinium dications. We now report practical approaches to these compounds, based on the method of Hünig and Köbrich[6] for the synthesis of 1-arylpyridones from arylamines and pyrones.

Pyridiniopyridones (4) *and* (5).—*Preparation.* 1-Aminopyridinium salts (1) and 4-oxopyran-2,6-dicarboxylic acid (2) in boiling conc. hydrochloric acid (48 h) gave the pyridiniopyridones (4) in good yield. The chloride hydrochlorides were isolated by precipitation with acetone, and although they could not be analysed satisfactorily, their structures were confirmed by i.r. and ^{1}H n.m.r. spectroscopy (see below). Treatment of the crude chlorides with ethanol and 40% tetrafluoroboric acid or ethanolic sodium perchlorate gave, respectively, the tetrafluoroborate and perchlorate salts (4; X = BF_4 or ClO_4). In this reaction, decarboxylation seems to occur spontaneously after attack by the 1-aminopyridinium salt. A reaction stopped after 16 h gave only unchanged starting materials, and some product (4). No trace of 2,6-dicarboxypyridiniopyridone was found.

4-Pyrone gave the pyridiniopyridone (4a) in high yield from compound (1a) under similar conditions, only with a much shorter heating time; the advantage of using the dicarboxylic acid (2) lies in its availability.

3-Acetyl-4-hydroxy-6-methyl-2-pyrone (3) similarly converted 1-aminopyridinium salts into the pyridiniopyridones (5), isolated as the chloride hydrochlorides after only 3 h heating time; a single reaction with the less readily available 2,6-dimethyl-4-pyrone also succeeded. The chloride hydrochlorides were converted into tetrafluoroborates or perchlorates as above.

Those 1-aminopyridinium salts with a substituent in the 2-position (series b and e) gave low yields (see Table 1); the 2,6-dimethyl derivative (1f) gave no isolable product. This is due presumably to steric effects, though in addition the much higher solubility of such products rendered isolation more difficult.

Dehydrobenzoylacetic acid, however, did not react with 1-aminopyridinium chloride, even when ethanol was added to increase solubility. Attempted reaction in a Carius tube at 150 °C for 15 h gave only 2,6-diphenyl-4-pyrone.

Spectroscopic properties (*Table* 2). I.r. spectra of pyridiniopyridone tetrafluoroborates (4) and (5) all show intense, broad peaks near 1 650 and 1 570—1 590 cm^{-1}; the latter are the stronger and are assigned, by analogy with 4-pyridones,[7] primarily to ν(C=O). The former (poorly resolved doublets) are assigned to pyridine and pyridone ν(C=C) ring modes. Spectra of pyridiniopyridones of type (4) possess a strong sharp band near 1 190 whereas strong absorption occurs for the dimethyl analogues (5) near 1 350 cm^{-1}. The peaks in the 650—850 cm^{-1} region listed in Table 2 are characteristic of the substitution patterns of the two rings.[8]

The ^{1}H n.m.r. spectra of the tetrafluoroborates

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[2] Preliminary communication, A. R. Katritzky and M. P. Sammes, *J.C.S. Chem. Comm.*, 1975, 247.
[3] See A. R. Katritzky and J. M. Lagowski, 'Chemistry of the Heterocyclic *N*-Oxides,' Academic Press, New York and London, 1971.
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[5] A. R. Katritzky and J. W. Suwinski, *Tetrahedron Letters*, 1974, 4123; *Tetrahedron*, 1975, **31**, 1549.
[6] von S. Hünig and G. Köbrich, *Annalen*, 1958, **617**, 181.
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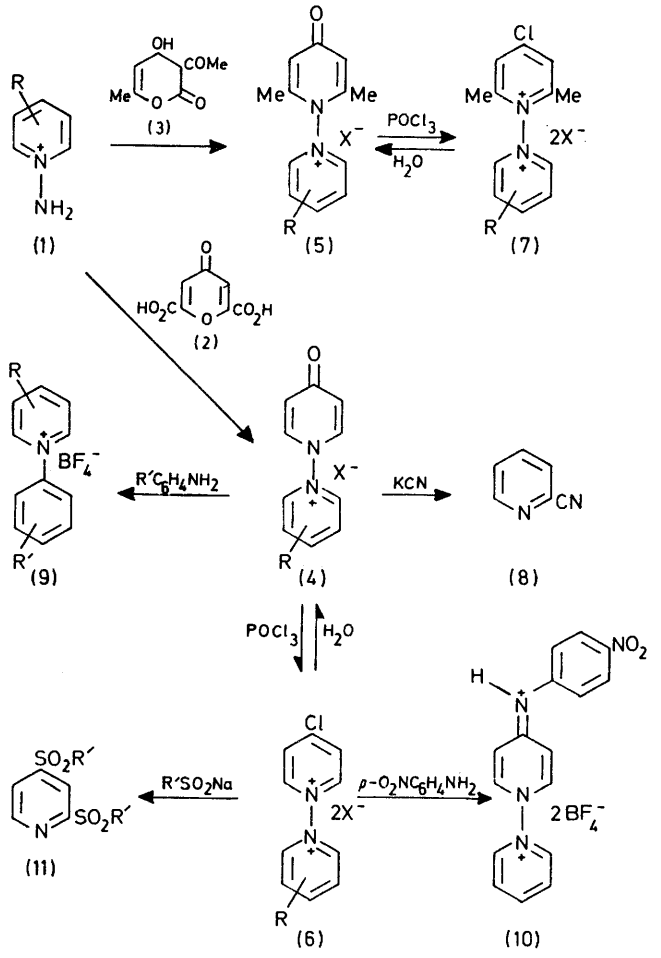
(Table 2) provide good evidence for the assigned structures: the peak positions and J values are as



R	R′
a; H	u. H
b; 2-Me	v. 4-Me
c; 3-Me	w. Me
d. 4-Me	x. Ph
e. 2-Me-5-Et	y. 4-MeC$_6$H$_4$
f. 2,6-Me$_2$	

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expected.[9] However, the positions of peaks due to protons on the pyridone nuclei are sensitive to traces of acid, and are shifted by up to 0.5 p.p.m. to lower field in the chloride hydrochloride salts, reflecting protonation at the carbonyl group.

All pyridiniopyridones show a principal u.v. absorption maximum near 260 nm, slightly shifted hypsochromically with a small decrease in $\varepsilon_{max.}$, on addition of hydrochloric acid. A broad shoulder near 290 nm (which disappears on addition of acid) is much reduced in intensity in the spectra of the 2,6-dimethyl derivatives (5), and essentially indistinguishable when an α-methyl group is present on the pyridinium ring, thus demonstrating sensitivity to the degree of coplanarity of the two rings.

Mass spectra of the pyridiniopyridones (4) and (5) all show a parent $M^{+\cdot}$ peak, together with a strong $M - 1$ peak. The fragmentation pattern is characterised by N–N cleavage leading to the corresponding pyridine [*m/e* 79 for the parent, 93 for the monomethyl derivatives, and 120 (rather than 121) for the series e] and a protonated pyridone (*m/e* 95 or, for the dimethyl derivatives, 123). The pyridine or the $M - 1$ ion is usually the base peak. This fragmentation is followed by normal degradation of the pyridines and of 4-pyridone.[10,†] The BF_2^+ gives an intense peak (*m/e* 48 and 49, ratio 1 : 4), but there is little evidence of ring fluorination [contrast (6) and (7), below].

Reactions. With saturated aqueous potassium cyanide, compound (4a; X = BF_4) gave 87% of 2-cyanopyridine (8) with a negligible amount of the 4-isomer. *N*-Alkoxypyridinium iodides with potassium cyanide give mixtures of 2- and 4-cyanopyridines,[11] the relative amounts depending upon the conditions,[12] whereas with 1-(*N*-acylalkylamino)pyridinium salts, attack of CN^- occurs predominantly in the 4-position.[13] A recent paper [14] discusses competition for the 2- and 4-positions of pyridinium salts by nucleophiles in terms of kinetic and thermodynamic factors.

N-Arylpyridinium salts in which the aryl group does not contain electron-withdrawing substituents are usually prepared by indirect methods, by reaction between an arylamine and an activated pyridinium salt,[15] a pyrylium salt,[16] or a furan derivative.[17] The pyridones (4) and (5) can be considered as activated pyridinium salts, and on heating with aniline and *p*-toluidine, (4a) gives the corresponding *N*-arylpyridinium salts (9au) and (9av) in good yield.

† The mass spectrum of 2,6-dimethyl-4-pyridone does not appear to have been reported previously. We find *m/e* 123 ($M^{+\cdot}$, 100%), 94 ($M^{+\cdot} - CO + H^{\cdot}$, 11), 84 ($M^{+\cdot} - C_3H_3^{\cdot}$, 18), 68 (6), 53 (8), 42 (8), and 39 (11.5). All seven peaks were prominent in the mass spectra of pyridiniopyridones of type (7).

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TABLE 1

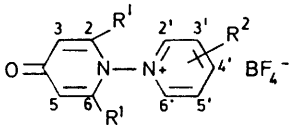
Physical and analytical data for new compounds

Compd.	X	Yield (%) [a]	M.p. (°C)	Cryst. form	Solvent [b]	Found (%) C	H	N	Formula	Required (%) C	H	N
(4a)	ClO_4		248—252 [d]	Plates	A + B	43.9	3.1	10.2	$C_{10}H_9ClN_2O_5$	44.1	3.3	10.3
(4a)	BF_4	78	232—234 [d]	Plates	A	45.8	3.7	10.7	$C_{10}H_9BF_4N_2O$	46.1	3.5	10.8
(4b)	BF_4	45	199—201 [d]	Prisms	A	47.8	4.0	10.2	$C_{11}H_{11}BF_4N_2O$	48.2	4.1	10.2
(4c)	ClO_4		238—243 [d]	Plates	A	45.9	4.1	9.4	$C_{11}H_{11}ClN_2O_5$	46.1	3.9	9.8
(4c)	BF_4	67	207—210 [d]	Plates	A	48.4	4.2	10.0	$C_{11}H_{11}BF_4N_2O$	48.2	4.1	10.2
(4d)	BF_4	70	199—200 [d]	Prisms	A	47.9	4.2	10.2	$C_{11}H_{11}BF_4N_2O$	48.2	4.1	10.2
(4e) [c]	BF_4	13	194—200 [d]	Plates	A	45.3	4.8	8.0	$C_{26}H_{31}B_3F_{12}N_4O_2$	45.1	4.5	8.1
(5a)	ClO_4	53	216—218 [d]	Needles	A	47.8	4.5	9.3	$C_{12}H_{13}ClN_2O_5$	47.9	4.4	9.3
(5a)	BF_4	79	203—206 [d]	Needles	A	49.6	4.6	9.9	$C_{12}H_{13}BF_4N_2O$	50.0	4.5	9.7
(5b)	BF_4	39	204—208 [d]	Plates	A	51.6	4.7	9.4	$C_{13}H_{15}BF_4N_2O$	51.7	5.0	9.3
(5c)	BF_4	75	211—213 [d]	Plates	A	51.5	5.1	9.1	$C_{13}H_{15}BF_4N_2O$	51.7	5.0	9.3
(5d)	BF_4	87	189—193 [d]	Needles	A	51.4	4.9	9.2	$C_{13}H_{15}BF_4N_2O$	51.7	5.0	9.3
(5e) [c]	BF_4	10	209—213 [d]	Plates	A	48.3	5.6	7.3	$C_{30}H_{39}B_3F_{12}N_4O_2$	48.3	5.2	7.5
(6a)	BF_4	80	197—201 [d]	Prisms	C	32.7	2.5	7.7	$C_{10}H_9B_2ClF_8N_2$	32.8	2.5	7.7
(6b)	BF_4	38	174—179 [d]	Needles	C + E	35.0	3.0	7.2	$C_{11}H_{11}B_2ClF_8N_2$	34.7	2.9	7.4
(6c)	BF_4	65	175—183	Prisms	C + E	35.0	2.9	7.4	$C_{11}H_{11}B_2ClF_8N_2$	34.7	2.9	7.4
(7a)	BF_4	63	163—169	Prisms	D + F	36.9	3.5	7.1	$C_{12}H_{13}B_2ClF_8N_2$	36.6	3.3	7.1
(7b)	BF_4	25	158—164	Prisms	A + C	38.4	3.8	6.9	$C_{13}H_{15}B_2ClF_8N_2$	38.2	3.7	6.9
(7c)	BF_4	40	166—172 [d]	Prisms	A + C	38.0	3.6	6.5	$C_{13}H_{15}B_2ClF_8N_2$	38.2	3.7	6.9
(7d)	BF_4	39	174—180	Plates	A + C	38.4	3.8	7.0	$C_{13}H_{15}B_2ClF_8N_2$	38.2	3.7	6.9
(9au)	BF_4	61	177—179	Plates	A	54.3	6.0	4.4	$C_{11}H_{10}BF_4N$	54.4	5.8	4.1
(9av)	BF_4	50	138—139	Needles	B	57.8	5.4	5.8	$C_{13}H_{14}BF_4N$	57.6	5.2	5.2
(10)	BF_4	90	251—254 [d]	Prisms	B	41.4	3.3	12.0	$C_{16}H_{14}B_2F_8N_4O_2$	41.1	3.0	12.0
(11w)		63	176—177	Prisms	A	35.8	3.9	6.1	$C_7H_9NO_4S_2$	35.7	3.9	6.0
(11x)		64	108—109	Needles	A	56.8	3.9	4.0	$C_{17}H_{13}NO_4S_2$	56.8	3.7	3.9
(11y)		52	139—140	Prisms	A	59.0	4.4	3.7	$C_{19}H_{17}NO_4S_2$	58.9	4.4	3.6

[a] Yields of salts (4)—(7) refer to the crude chloride prior to conversion into tetrafluoroborate or perchlorate. [b] Solvents: A, EtOH; B, H_2O; C, MeCN; D, Et_2O; E, PhH; F, Me_2CO. [c] Analysis as required for the 0.5 HBF_4 derivative. [d] With decomposition.

TABLE 2

^1H N.m.r., i.r., and u.v. spectroscopic data for compounds (4) and (5)



Compd.	δ [a] Substituent position [b] 2,6 [c]	3,5	2′	3′	4′	5′	6′	Principal common i.r. bands (cm^{-1}) [d]				$\lambda_{max.}$/nm (log ε)				
(4a)	8.24	6.66	9.42	8.40	8.98	8.40	9.42	1 656	1 583	1 189	856	785 [e]			262	276 [f] 290 [g]
								1 633				678			(4.40)	(4.11) (3.83)
(4b)	8.29	6.87	*2.77*	8.25	8.83	8.2	9.24	1 657	1 592	1 188	854	784			267	275
								1 649				702			(4.34)	(4.18)
(4c)	8.25	6.69	9.27	*2.68*	8.78	8.29	9.23	1 656	1 590	1 191	855	802			266	275 292
								1 640		1 183		678			(4.28)	(4.15) (3.65)
(4d)	8.35	6.71	9.20	8.24	*2.85*	8.24	9.20	1 658	1 590	1 188	850	837		229	263	275 290
								1 640				705		(3.98)	(4.36)	(4.11) (3.93)
(4e)	8.23	6.84	*2.71*	8.19	8.70	*1.33*	9.09	1 660	1 599	1 189	858	844		220	269	275
						2.96		1 642				704		(3.73)	(4.25)	(4.19)
(5a)	*2.10*	6.55	9.44	8.58	9.13	8.58	9.44	1 653	1 577	1 350	880	786	212		262	290
												384	(4.23)		(4.45)	(3.15)
(5b)	*2.08*	6.63	*2.73*	8.41	8.92	8.38	9.27	1 657	1 581	1 354	877	798	213		265	
								1 649				717	(4.12)		(4.34)	
(5c)	*2.12*	6.52	9.2	*2.73*	8.91	8.41	9.2	1 655	1 580	1 351	879	806	211		264	300
								1 648				681	(4.23)		(4.45)	(3.15)
(5d)	*2.13*	6.52	9.18	8.34	*2.90*	8.34	9.18	1 658	1 561	1 359	872	830	215	229	263	273 298
								1 650				710	(4.15)	(4.00)	(4.40)	(4.15) (3.15)
(5e)	*2.16*	6.85	*2.68*	8.34	8.84	*1.37*	9.12	1 656	1 574	1 354	888	864	213		266	280
						3.02		1 646				710	(4.18)		(4.18)	(3.85)

[a] In D_2O. Values given to one decimal place are approximate. [b] Values in italics are for alkyl substituents. [c] In type (4) compounds J *ca.* 8 Hz. [d] All tetrafluoroborate salts show a broad intense peak near 1 060 cm^{-1} (BF_4^-). [e] Absorptions characteristic of pyridine ring substitution pattern. [f] Values in this column refer to poorly resolved points of inflection. [g] Values in this column refer to a broad shoulder.

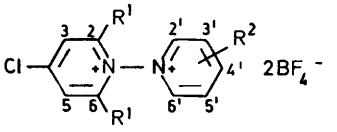
Pyridiniopyridinium Salts (6) *and* (7).—*Preparation.* The parent pyridiniopyridone (4a) is converted into the pyridiniopyridinium chloride (6a) in high yield by boiling in phosphoryl chloride. The method also converts the 3-methyl derivative (4c) into the salt (6c). However, when an α- or γ-methyl group is present in either ring the pyridiniopyridone dissolves completely with evolution of hydrogen chloride, and the resulting solution on addition of dry ether, or on removal of reagent under reduced pressure, yields only polymeric material. Probably, proton loss from the side chain methyl group occurs, followed by attack by chloride ion and disruption of the system.

reprecipitating with either ethanol or benzene. Compound (7a) formed solvates with acetonitrile, ethanol, and acetone, but was recrystallised by dissolving in dry acetone, and adding dry ether.

Spectroscopic data. The principal common i.r. bands are given in Table 3. The band near 1 625 cm^{-1} is much sharper than that near 1 650 cm^{-1} in the spectra of the pyridiniopyridones (Table 2), and the peak assigned to ν(C=O) in the latter is replaced by a sharper, weaker absorption at lower frequency (protonation of the pyridiniopyridones, as in the chloride hydrochloride salts, leads to similar changes in the i.r. spectra). New, common, sharp bands are found in the spectra of all

TABLE 3

^{1}H N.m.r. and i.r. spectroscopic data for compounds (6) and (7)



Compd.	δ [a] Substituent position [b] 2,6	3,5	2′	3′	4′	5′	6′	Principal common i.r. bands (cm^{-1}) [c]						
(6a)	9.4	8.4	9.5	8.5	9.13	8.5	9.5	1 626	1 553w	1 490	1 286	1 127	839 [d]	787 [d] 679
(6b)	9.41	8.56	*2.83*	8.31	8.93	8.31	9.31	1 628	1 553w	1 481	1 282	1 127	851	786 697
(6c)	9.44	8.46	9.31	*2.81*	8.91	8.4	9.4	1 631	1 556w	1 502	1 293	1 128	851	808 682
(7a) [e]	*2.66*	8.13	9.52	8.80	9.25	8.80	9.52	1 624	1 559	1 492	1 290		891	787 679
(7b)	*2.65*	8.25	*2.80*	8.61	9.09	8.61	9.33	1 624	1 560	1 501	1 293		894	786 702
(7c)	*2.65*	8.13	9.28	*2.86*	9.06	8.64	9.31	1 627	1 567	1 506	1 292		902	806 680
(7d)	*2.64*	8.11	9.26	8.51	*3.02*	8.51	9.26	1 625	1 561	1 501	1 292		892	829

[a] In CF_3CO_2H. Values given to one decimal place are approximate. [b] Values in italics are for alkyl substituents. [c] All tetrafluoroborate salts show a broad intense peak near 1 060 cm^{-1} (BF_4^-). [d] Absorptions characteristic of pyridine ring substitution pattern. [e] Heating at 80 °C and 0.1 mmHg was necessary to remove the last traces of acetone.

The pyridiniopyridones (4b) and (5) yield pyridiniopyridinium chlorides (6b) and (7) on stirring vigorously at room temperature with phosphoryl chloride–phosphorus pentachloride. With the exceptions of the pyridone (5b), which gives essentially pure product (7b), and of the pyridone (4d), which did not react, all such reactions gave a suspension of starting material (≤35%) mixed with pyridiniopyridinium salt. Addition of dry ether to the filtrate precipitated more pyridiniopyridinium chloride. The yields recorded in Table 1 refer to the amounts of pyridiniopyridinium chloride detected in the mixtures by ^{1}H n.m.r. spectroscopy. The success of this conversion seems to require an appreciable solubility of the pyridiniopyridone in phosphoryl chloride at a temperature low enough to discourage side reactions.

The crude chlorides (6 and 7; X = Cl) could be converted into pure tetrafluoroborates (6 and 7; X = BF_4) by stirring with ice-cold 40% tetrafluoroboric acid and then adding absolute ethanol. The tetrafluoroborates were recrystallised by taking up in dry acetonitrile, and seven pyridiniopyridinium salts near 1 500 and near 1 290 cm^{-1}.

All bands in the ^{1}H n.m.r. spectra of the pyridiniopyridinium salts are shifted to lower field relative to the pyridiniopyridones, especially for protons in the chloropyridinium ring (see Table 3).

None of the pyridiniopyridinium salts shows a parent $M^{+\cdot}$ peak in the mass spectrum. The principal peaks arise from cleavage of the N–N bond, giving pyridine {*m/e* 79 or 93 [except the 2-methyl derivative (6b) which gives *m/e* 92]}, chloropyridine (*m/e* 113 and 115, or for the dimethyl compounds 141 and 143), and their respective degradation products. However, the chloropyridine fragment seems to be susceptible to monofluorination (prominent peaks at *m/e* 131 and 133, or 159 and 161), but these are absent in the spectrum of the 2-methyl derivative (6b). The pyridine fragment lacking the chlorine atom is less susceptible to fluorination, though compound (6a) shows a strong peak at *m/e* 97 and compound (6b) at *m/e* 111. As with pyridiniopyridones, BF_2^+ is observed at *m/e* 48 and 49 (ratio 1 : 4).

Reactions. Compounds of both types (6) and (7) are hydrolysed by water to the respective pyridiniopyridones (4) and (5). Those of type (6) are more labile: thus 10% solutions of compounds (6a) and (7a) in D_2O at 34 °C after 45 min are hydrolysed respectively to the extent of 75 and 15% (by ^1H n.m.r.). The chlorides (6a and 7a; X = Cl) are much more hygroscopic than the corresponding tetrafluoroborates.

The chlorine atom of the pyridiniopyridinium salt (6a; X = BF_4) is displaced almost quantitatively by *p*-nitroaniline in refluxing ethanol to give the derivative (10). It is thus possible to substitute the group in the 4-position without cleaving the N–N bond.

Trituration of the pyridiniopyridinium chloride (6a; X = Cl) with aqueous 20% solutions of the sodium salts of the corresponding sulphinic acids gives good yields of the sulphones (11). These represent the first examples of pyridine rings bearing two sulphone residues. Initial attack probably occurs in the 4-position with the displacement of chloride ion, since no 4-chloro-2-sulphonylpyridines were found. Mass spectra of sulphones all showed a base peak at $M - 64$.

The synthetic potential of pyridiniopyridones and pyridiniopyridinium salts with respect to attack by a wide range of nucleophiles is being evaluated.

EXPERIMENTAL

I.r. spectra were recorded in Nujol on a Perkin-Elmer 577 spectrophotometer, u.v. spectra in absolute ethanol on a Unicam SP 800 spectrophotometer, ^1H n.m.r. spectra on a Perkin-Elmer R-20 spectrometer, and mass spectra on a Hitachi RMS-4 spectrometer. Spectroscopic data are presented in Tables 2 and 3, and physical and microanalytical data for the new compounds in Table 1.

4-Pyrone,[18] 4-oxopyran-2,6-dicarboxylic acid (2),[19] 2,6-dimethyl-4-pyrone,[20] 3-acetyl-4-hydroxy-6-methyl-2-pyrone (3),[21] dehydrobenzoylacetic acid,[22] and sodium methanesulphinate [23] were prepared by known methods.

Preparation of 1-*Aminopyridinium Salts* (1).—The method of Gösl and Meuwsen [24] was modified as follows to give the chlorides (0.3 mol scale). The product from addition of anhydrous K_2CO_3 was filtered, and the filtrate extracted with ether (5 × 50 ml) to remove the excess of pyridine. The aqueous layer was evaporated as far as possible (30—40 °C *in vacuo*); absolute EtOH (350 ml) was added to the residue and the resulting suspension filtered. Hydrochloric acid (36%; 30 ml) was added cautiously to the filtrate, which was evaporated to dryness (100 °C *in vacuo*). The crude *chlorides* (hygroscopic) were used in this form; yields: (1a) 77%; (1b) 56%; (1c) 67%; (1d) 72%; (1e) 35%; (1f) 23%.

1-*Pyridinio*-4-*pyridones* (4).—4-Oxopyran-2,6-dicarboxylic acid (2) (0.03 mol) and the appropriate 1-aminopyridinium salt (1) (0.03 mol) were heated under reflux in conc. HCl (15 ml) for 48 h. The product was stirred with charcoal (1 g), cooled in ice, and filtered, and the filtrate was evaporated to dryness. Trituration of the residue with dry Me_2CO (4 × 50 ml) gave a crystalline solid which was taken up in conc. HCl (10 ml); the mixture was filtered and the filtrate added to dry Me_2CO (500 ml). The suspension was stirred overnight and filtered, and the residue washed with dry Me_2CO to give the desired *pyridiniopyridone* as the chloride hydrochloride. A saturated solution in absolute EtOH, on treating with 40% HBF_4 gave the corresponding tetrafluoroborate (4; X = BF_4).

Substitution of 4-pyrone for the acid (2) in the reaction with the 1-aminopyridinium salt (1a) gave the pyridone (4a) (90%), in only 2 h.

2,6-*Dimethyl*-1-*pyridinio*-4-*pyridones* (5).—These were prepared and isolated as described for the pyridones (4), with 3-acetyl-4-hydroxy-6-methyl-2-pyrone (3) being used in place of the acid (2), and the heating time being reduced to 3 h. Compound (5e) did not solidify as the chloride, and appeared to be appreciably soluble in Me_2CO. It was converted directly into the tetrafluoroborate.

Substitution of 2,6-dimethyl-4-pyrone for the 2-pyrone (3) in the reaction with compound (1a) gave the pyridone (5a) in 30% yield.

4-*Chloropyridiniopyridinium Salts* (6) *and* (7).—*Method A.* The dry pyridiniopyridone (0.004 mol; as the chloride hydrochloride) and $POCl_3$ (10 ml) were heated together under reflux for 15 min. The product was cooled, filtered under a rubber dam, and washed with $POCl_3$ (20 ml) and then ether (3 × 10 ml; anhydrous). Compounds (4a and c) gave the products (6a and c) as *dichlorides* (X = Cl); other pyridones dissolved completely to give polymeric materials.

Method B. The dry pyridiniopyridone (0.004 mol; as the chloride hydrochloride) was stirred vigorously with $POCl_3$ (40 ml) and PCl_5 (0.001 mol) for 72 h at 30 °C in a stoppered flask. The product was filtered and the residue washed as in method A to give a mixture of starting material and the desired chloropyridiniopyridinium dichloride. Addition of anhydrous ether (100 ml) to the filtrate, with vigorous stirring, precipitated purer chloropyridiniopyridinium salt. Compound (4d) did not react.

Conversion of Chloropyridiniopyridinium Chlorides into Tetrafluoroborates.—The crude chlorides, containing up to 35% pyridiniopyridone (6 and 7; X = Cl) (0.001 mol) were triturated with ice-cold HBF_4 (1 ml; 40%), and EtOH (10 ml) was added. The resulting suspensions were filtered, and the residues washed with absolute EtOH and then anhydrous ether. The products were recrystallised by dissolving in the minimum dry MeCN, filtering, and diluting the vigorously stirred filtrates with dry benzene [type (6)] or absolute EtOH [type (7)]. Recovery varied between 30 and 75%.

Reaction of the Pyridiniopyridone (4a; X = BF_4) *with Potassium Cyanide.*—Saturated aqueous KCN (3 ml) was added all at once to the pyridiniopyridone (0.002 mol) in water (2 ml). The mixture was kept at 20 °C for 2 h, during which the initially formed dark red colour faded. The product was then extracted with $CHCl_3$ (3 × 15 ml), the extracts were dried ($MgSO_4$), and the solvent was removed to give 2-cyanopyridine (8) (87%), m.p. *ca.* 26 °C

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(lit.,[25] 29 °C), identified by comparison (i.r. and ^1H n.m.r.) with an authentic sample.

Preparation of the Pyridinium Salts (9).—The appropriate pyridiniopyridone (4; X = BF_4) (0.001 mol) and aromatic amine (5 ml) were heated under reflux for 10 min. The excess of amine was removed by azeotropic distillation with water (2 × 50 ml), and the residue shaken with water (50 ml) and $CHCl_3$ (20 ml). The aqueous layer was extracted with $CHCl_3$ (10 ml), and evaporated to dryness. The residue was recrystallised from EtOH to give the corresponding *arylpyridinium tetrafluoroborate* (9).

Preparation of Compound (10).—The pyridiniopyridinium salt (6a; X = BF_4) (0.000 5 mol) and *p*-nitroaniline (0.001 mol) were heated together under reflux in absolute EtOH (5 ml) for 10 min. The cooled solution was filtered, and the residue washed with EtOH (5 ml) and then with ether (10 ml) to give 4-(p-*nitrophenylamino*)*pyridiniopyridinium bistetrafluoroborate* (10), M · 294; $\nu_{max.}$ 3 290 (NH), 1 542, 1 360 (NO_2), and 1 055 cm^{-1} (BF_4); δ [$(CD_3)_2NCDO$] 9.96 (2 H, d, *J* 5.5 Hz), 9.2 (3 H, m), 8.8—8.3 (4 H, m), and 7.8 (4 H, m).

Preparation of the Disulphones (11).—20% Sodium benzenesulphinate (3 ml) was added to the pyridiniopyridinium salt (6a; X = Cl) (0.000 5 mol). The resulting sticky mass was triturated with water for 20 min, diluted with water (10 ml), and extracted with ether (25 ml). The extract was washed (5% $NaHCO_3$ and water), dried ($MgSO_4$), and evaporated. The gummy residue was recrystallised from EtOH to give the *disulphone* (11x); $M^{+\cdot}$ 359; $\nu_{max.}$ 1 330, 1 315, 1 306, and 1 135 cm^{-1}; δ ($CDCl_3$) 8.85 (1 H, d, *J* 5 Hz), 8.60 (1 H, s), 8.0 (5 H, m), and 7.6 (6 H, m). Similarly prepared from sodium methanesulphinate was the *disulphone* (11w); $M^{+\cdot}$ 235; $\nu_{max.}$ 1 310 and 1 145 cm^{-1}; δ ($CDCl_3$) 8.96 (1 H, d, *J* 5 Hz), 8.50 (1 H, s), 8.0 (1 H, d, *J* 5 Hz), 3.28 (3 H, s), and 3.13 (3 H, s); and from sodium toluene-*p*-sulphinate the *disulphone* (11y); $M^{+\cdot}$ 387; $\nu_{max.}$ 1 329 and 1 152 cm^{-1}; δ ($CDCl_3$) 8.77 (1 H, d, *J* 5 Hz), 8.52 (1 H, s), 7.85 (5 H, m), 7.3 (4 H, m), and 2.41 (6 H, s).

Preparation of the Disulphone (11w) *from the Tetrafluoroborate Salt* (6a; X = BF_4).—The chloropyridiniopyridinium salt (0.000 3 mol) was suspended in water (1 ml) and a 20% solution of sodium methanesulphinate (1 ml) added. The brown solution was scratched for 5 min, diluted with water (10 ml), and filtered to give the disulphone (11w) (95%) essentially pure.

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