Nucleophilic Displacements of *N*-Aryl and Heteroaryl Groups. Part 4.[1] Pyrylium-mediated Transformations of Heteroarylamines into Pyridinium Salts and their Inter- and Intra-molecular Displacement

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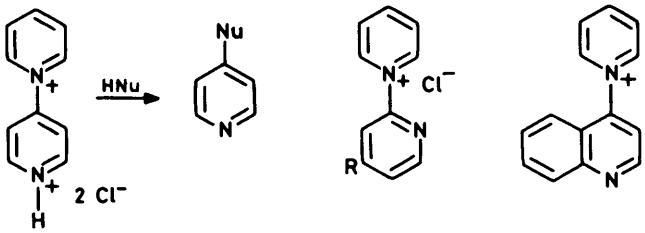
Heteroarylamines and the appropriate pyrylium salts give 1-heteroaryl-2-ethoxycarbonyl-4,6-diphenylpyridinium, and 1-(2-pyridyl)-2,6-diethoxycarbonyl-4-phenylpyridinium salts. Hydrolysis and decarboxylation afford 1-(2-pyridyl)-2,4-diphenyl- and 1-(2-pyridyl)-4-phenyl-pyridinium salts. Neither these, nor their 2,4,6-triphenyl analogues underwent smooth nucleophilic substitution.

1-Pyrimidin-2-yl- and 1-(4,6-dimethylpyridimidin-2-yl)-2-ethoxycarbonyl-4,6-diphenylpyridinium with ethanolic NaOEt smoothly formed the corresponding pyrimidin-2-ones *via* intramolecular attack.

Simultaneously with our investigation of possible transformations of arylamines mediated by pyrylium salts,[1-3] we have also investigated heteroarylamines. In some ways, such a process could be even more valuable than that for arylamines. Thus, whereas the diazonium reaction allows the facile transformation of arylamines into many other types of functionality,[4] it is less easily applied to heteroarylamines. Although the diazotization of amino groups α- and γ- to a pyridine-like nitrogen atom can be effected in concentrated acids,[5] the diazonium derivatives are unstable and easily decompose to the corresponding hydroxy compounds (which readily tautomerize to pyridones, *etc.*);[6] however, in the presence of halide ions the corresponding halide can be formed.[7] Non-aqueous diazotization can also be used to introduce halogens into pyridines.[8]

Many α- and γ-aminoheteroaromatics are readily available, and there is considerable literature precedent to suggest that an approach involving displacement of a pyridinium leaving group might be successful: Jerchel *et al.*[9,10] found that 1-(4-pyridyl)pyridinium chloride (1) with various nucleophiles gave the corresponding 4-substituted pyridines (2). Recently this method has been used to prepare pyridine-4-phosphonic acids [11] and 4-pyridyl sulphides.[12] Pyridine has functioned as a leaving group in other *N*-heteroaryl systems, including 2-pyridyl (3) [12,13] and (4),[11] 4-quinolyl (5) [14] and acridin-9-yl derivatives.[15] However, such reactions sometimes take a different course, with attack of the nucleophile at the α-position of the pyridinium ring.[15,16]

We now describe our initial results of attempting to extend our pyrylium-mediated transformations of aliphatic primary amines to these derivatives. During the course of this investigation we became aware of the elegant work of Taylor *et al.*[17] who have converted heteroaromatic amino groups *via* sulphilimines and nitroso compounds into nitro derivatives which undergo easy nucleophilic displacements.



(1) (2) (3) R = Me (4) R = H (5)

(6) R = 2-Pyridyl
(7) R = 4-Pyridyl
(8) R = Benzothiazol-2-yl
(9) R = Pyrimidin-2-yl

(10)

1-Heteroaryl-2,4,6-triphenylpyridinium Salts.—2,4,6-Triphenylpyrylium tetrafluoroborate with the appropriate heteroarylamines gave the corresponding pyridinium tetrafluoroborates (6)—(9) in good yields (Table 1). For the preparation of the pyrimidin-2-yl derivative (8), triethylamine was used as a catalyst.[18] Structures were confirmed by spectral data (Tables 2 and 3). The ^{1}H n.m.r. spectra showed the expected singlets for the pyridinium 3,5-protons, with multiplets for the other aryl signals.

We have previously shown that *N*-heteroaryl-2,4,6-triphenylpyridinium iodides successfully give heteroaryl iodides on pyrolysis,[19] and this suggested that other soft nucleophiles might react likewise. However, although pyrolysis of the tetrafluoroborate (7) with sodium dimethyldithiocarbamate (a reaction which proceeds well with *N*-alkyl-2,4,6-triphenylpyridinium salts [20]) gave the novel 4-pyridyldithiocarbamate (10); only mixtures were produced from the other *N*-heteroarylpyridinium salts (6)—(9) on similar treatment.[21]

Models indicate that the 1-heteroaryl substituent and the 2- and 6-phenyl groups of a 1-heteroaryl-2,4,6-triphenylpyridinium salt all lie approximately perpendicular to the plane of the central pyridinium ring. Hence, the approach of a nucleophile perpendicular to the plane of the heteroaryl substituent ring, as required in a normal substitution, is severely hindered. We therefore turned our attention to the preparation of 1-heteroaryl-2,4-diphenylpyridinium salts in which such nucleophile approach should be easier.

1-Heteroaryl-2,4-diphenylpyridinium Salts.—2,4-Diphenylpyrylium salts are readily available,[22] but do not react readily with amines to give pyridinium salts.[21] Although 2-carboxy-4,6-diphenylpyrylium perchlorate (11) with aniline gave 1,2,4-triphenylpyridinium perchlorate (13) in good yield, (11) did not

Table 1. Preparation of pyridinium tetrafluoroborates

Compd.	Method	Solvent	Time (h)	Yield (%)	M.p. (°C)	Crystal form	Found (%) C	H	N	Molecular formula	Required (%) C	H	N
(6)	A	EtOH	2	80	232—234 [a]	Prisms	71.0	4.4	5.9	$C_{28}H_{21}BF_4N_2$	71.1	4.4	5.9
(7)	A	EtOH	2	75	207—208	Prisms	70.3	4.4	5.8	$C_{28}H_{21}BF_4N_2$	71.1	4.4	5.9
(8)	A	EtOH	2	85	258—260	Prisms	68.0	3.9	5.3	$C_{30}H_{21}BF_4N_2S$ [b]	68.2	4.0	5.3
(9)	B	EtOH	12	84	262—264	Needles	68.1	4.4	8.8	$C_{27}H_{20}BF_4N_3$	68.5	4.2	8.9
(15)	C	CH_2Cl_2	0.50	97	186—187	Needles	59.3	4.5	3.0	$C_{26}H_{22}BF_4NO_2$	59.4	4.7	3.0
(16)	D	CH_2Cl_2	0.25	70	192—193	Needles	63.9	4.5	5.9	$C_{25}H_{21}BF_4N_2O_2$	64.1	4.5	6.0
(17)	D	CH_2Cl_2	0.25	50	187—188	Needles	62.6	4.3	8.3	$C_{24}H_{20}BF_4N_3O_2$	61.4	4.3	8.9
(18)	C	CH_2Cl_2	0.50	70	192—194	Needles	62.3	4.6	8.2	$C_{26}H_{24}BF_4N_3O_2$	62.7	4.8	8.4

[a] Lit. m.p. 233 °C (A. R. Katritzky, U. Gruntz, A. A. Ikizler, D. H. Kenny, and B. P. Leddy, *J. Chem. Soc., Perkin Trans. 1*, 1979, 436. [b] Analysis for S found 6.09%, required 6.06%.

Table 2. ^{1}H N.m.r. spectral data [a] of pyridinium salts

Compd.	3-H δ	m	J	5-H δ	m	J	Protons on *N*-substituent δ	H	m	J	Other protons δ	H	m	J	CO_2Et δ	H	m	J
(6)	8.64	s	—	8.64	s	—	8.40	1	d	6	7.62	5	m	—			—	
							8.34	3	m	—	7.34	10	m	—				
(7)	8.62	s	—	8.62	s	—	8.32	4	m	—	7.40	5	m	—			—	
												10	m	—				
(8)	8.76	s	—	8.76	s	—	8.40	2	m	—	7.64	10	m	—			—	
							7.88	2	m	—	7.39	5	m	—				
(9)	8.72	s	—	8.72	s	—	8.72	2	d	6	7.60	6	m	—			—	
							8.34	1	m	—	7.40	9	m	—				
(15)	8.36	d	2	8.04	d	2	7.46—7.29	5	m	—	7.80	2	m	—	4.24	2	q	6
											7.46—7.29	8	m	—	0.98	3	t	6
(16)	8.42	d	2	8.75	d	2	8.62	1	dd	2,6	8.02	2	m	—	4.24	2	q	6
							7.66	3	m	—	7.50—7.34	8	m	—	1.16	3	t	6
(17)	8.40	d	2	8.72	d	2	8.70	2	d	6	7.95	2	m	—	4.34	2	q	6
							7.65	1	m	—	7.65—7.20	8	m	—	1.30	3	t	6
(18)	8.40	d	2	8.82	d	2	7.70	1	m	—	7.90	2	m	—	4.40	2	q	6
							2.48	6	s	—	7.70	1	m	—	1.30	3	t	6
											7.40	7	m	—				

[a] δ[$(CD_3)_2SO$], *J* in Hz.

react satisfactorily with heteroarylamines.[21] However, the pyrylium ester tetrafluoroborate (12) [23] gave with aniline and with several heteroarylamines good yields of the corresponding *N*-phenyl (15) and *N*-heteroaryl substituted pyridinium tetrafluoroborates (16)—(18) (Table 1); in some cases NEt_3 was used to catalyze the reaction.[18] The products (15)—(18) were characterised by their spectra (Tables 2 and 3). The characteristic finely split doublet pattern is shown for the 3,5-protons of the pyridine ring; the other aryl signals give the expected multiplets and the characteristic A_2X_3 pattern is found for the CO_2Et group.

When the *N*-phenyl derivative (15) was heated with hydrogen chloride in acetic acid, 1,2,4-triphenylpyridinium tetrafluoroborate (13) (60%) was formed. However, the *N*-2-pyridyl derivative (16) was unaffected by this treatment, and ethanolic ammonia converted (16) into 2-carbamoyl-4,6-diphenylpyridine (19) by an ANRORC reaction and simultaneous amide formation (*cf.* ref. 24). Compound (16) with hot ethanolic sodium hydroxide gave the desired 2,4-diphenyl-1-(2-pyridyl)pyridinium tetrafluoroborate (14), whereas with cold aqueous NaOH, (16) yielded the betaine (20) [ν(C=O) at 1 650 cm^{-1}]. The betaine (20) underwent decarboxylation in hot alcohols to give the ethoxy- (21) and methoxy-dihydropyridines (22). In these dihydropyridines, (21) and (22), the pyridine ring protons had moved to the vinylic region (δ 6—7) and the expected signals for OMe and OEt were present.

Attempted reactions of the pyridinium tetrafluoroborate (14) with a variety of nucleophiles either failed completely or gave complex mixtures of products.[21]

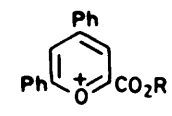
Preparation and Reactions of 1-(2-*Pyridyl*)-4-*phenylpyridinium Salts.*—It seemed possible that the unreactivity of the α-phenylpyridinium (14) towards nucleophiles could be due to the α-substituent, and we therefore addressed ourselves to the α,α-unsubstituted series. 2,6-Diethoxycarbonyl-4-phenylpyrylium tetrafluoroborate (23) with 2-aminopyridines gave [25] the pyridinium (24) which was de-ethoxycarbonylated using the t-butylamine method [24] to give (28). However, repeated attempts to effect a nucleophilic displacement on (28) with thiourea failed: it has been reported that such reactions give poorer yields in the 2- than in the 4-pyridyl series.[12]

Preparation of Pyrimidin-2-ones via *Intramolecular Nucleophilic Attack in* 2-*Ethoxycarbonyl*-1-*pyrimidin*-2-*ylpyridinium Salts.*— Success was finally achieved, at least in the pyrimidine series, under surprisingly mild conditions. The 2-ethoxycarbon-

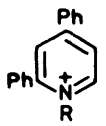
Table 3. I.r. spectral data of pyridinium salts

Compd.	νC=O	Pyridinium and phenyl rings ν(C–C) [a]	BF_4	Finger print region	γ(C–C) (Py^+) [b]	γ(C–H) (Py^+, Ph)
(6)		1 620, 1 600, 1 550, 1 490, 1 470	1 050	1 430, 1 410, 1 355, 1 310, 1 290, 1 250	765	890, 780, 690
(7)		1 625d, 1 600, 1 585, 1 550, 1 500, 1 460, 1 450	1 050	1 410, 1 360, 1 285, 1 240, 1 180	765, 740	900, 840, 825, 780, 690
(8)		1 620, 1 598, 1 550, 1 490	1 050	1 420d, 1 360, 1 315, 1 295, 1 230br	760, 730	890, 690
(9)		1 620, 1 600, 1 580, 1 550, 1 490, 1 460	1 050	1 430, 1 400, 1 355, 1 290, 1 240, 995d	765, 750	895, 840, 825, 800, 690
(15)	1 750	1 625, 1 600, 1 560, 1 500, 1 470	1 050	1 380, 1 360, 1 255	765	900, 860, 690
(16)	1 750	1 620, 1 600, 1 580, 1 565, 1 460	1 050	1 445, 1 430, 1 375, 1 350, 1 290d, 1 260, 1 180	740d, 765d	900, 790, 690
(17)	1 740	1 610, 1 595, 1 580, 1 550, 1 490, 1 450	1 050	1 390d, 1 350, 1 290, 1 250	765	900, 850, 820, 690
(18)	1 750	1 620, 1 605, 1 550, 1 525, 1 490, 1 450	1 050	1 375, 1 350, 1 315, 1 265, 1 245, 1 200, 1 000	760, 750, 740	890, 850, 830, 795 785, 775, 710, 695

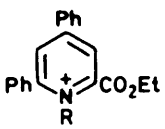
[a] ν = stretching. [b] γ = out-of-plane bending.



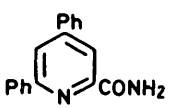
(11) R = H
(12) R = Et



(13) R = Ph
(14) R = 2-Pyridyl



(15) R = Ph
(16) R = 2-Pyridyl
(17) R = 4-Pyrimidin-2-yl
(18) R = 4′,6′-Dimethylpyrimidin-2-yl



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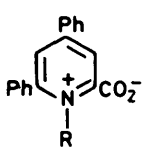
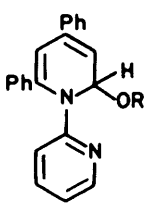
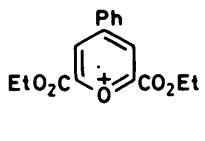


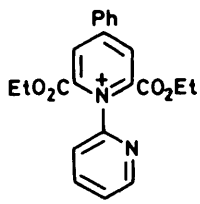
(20)



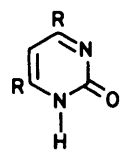
(21) R = Et
(22) R = Me



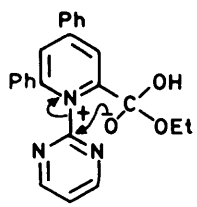
(23)



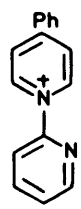
(24)



(25) R = H
(26) R = Me



(27)



(28)

yl-1-pyrimidin-2-ylpyridinium (17) with hot ethanolic EtONa gave pyrimidin-2-one (25) (50%) (characterised by its n.m.r. spectrum and as the picrate), together with 2-ethoxycarbonyl-4,6-diphenylpyridine. The 4,6-dimethylpyrimidin-2-yl analogue (18) similarly yielded 4,6-dimethylpyrimidin-2-one (26) (65%).

In view of the evidence mentioned above, the conversions (17) ⟶ (25) and (18) ⟶ (26) cannot be simple nucleophilic displacements. We believe that initial attack at the ethoxycarbonyl group is followed by intramolecular displacement, *cf.* (27). Although these conditions failed for the pyridine analogue (16), a general procedure was later discovered, see following paper.[26]

Experimental

M.p.s were obtained on a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were run using NaCl plates on a Perkin-Elmer 257 grating i.r. spectrophotometer, in $CHBr_3$ solution. ^1H N.m.r. spectra were run on a Perkin-Elmer 60 MHz R12 permanent magnet spectrometer or a Varian 100 MHz HA-100 spectrometer, with $SiMe_4$ as the internal standard.

The following compounds were made using literature methods: 2,4,6-triphenylpyrylium tetrafluoroborate, m.p. 253 °C (lit.,[27] m.p. 253—255 °C); 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (12), m.p. 156—157 °C (lit.,[23] m.p. 155—157 °C); 2,6-diethoxycarbonyl-4-phenyl-1-(2-pyridyl)pyridinium tetrafluoroborate (24), m.p. 215—216 °C (lit.,[25] m.p. 218—219 °C); 2,6-diethoxycarbonyl-4-phenylpyrylium tetrafluoroborate (23), m.p. 143—145 °C (lit.,[25] m.p. 143—145 °C).

2-Carboxy-4,6-diphenylpyrylium perchlorate (11) (15%) (m.p. 240 °C; lit.,[28] no m.p. given) was prepared by heating benzylidenepyruvic acid (10 mmol), acetophenone (10 mmol), and perchloric acid (10 ml) at 100 °C for 15 min, cooling the mixture and pouring it into ether.

General Methods for the Preparation of 1-*Substituted* 2,4,6-*Triphenylpyridinium Tetrafluoroborates* (6)—(9).—*Method A.* 2,4,6-Triphenylpyrylium tetrafluoroborate (0.01 mol) and the amine (0.02 mol) were heated in absolute EtOH (30 ml) under reflux for the appropriate time (Table 1). After cooling and trituration with Et_2O, the resulting white solid was filtered off and recrystallised from absolute EtOH to give the pyridinium tetrafluoroborate. Table 1 for physical and Tables 2 and 3 for spectral data.

Method B. As above but with the addition of NEt_3 (0.10 mol).

Pyrolysis of 2,4,6-*Triphenyl*-1-(4-*pyridyl*)*pyridinium Tetrafluoroborate* (7) *with Sodium Dimethyldithiocarbamate.*—An intimate mixture of the 1-(4-pyridyl)pyridinium tetrafluoroborate (7) (1 g, 2.0 mmol), sodium dimethyldithiocarbamate dihydrate (0.45 g, 3.0 mmol) and 2,4,6-triphenylpyridine [27] (0.65 g, 2.0 mmol) was pyrolysed at 235—240 °C/0.1 mmHg for 3 h in an apparatus connected to a liquid N_2 cooled trap. The contents of the trap were extracted in CH_2Cl_2 (10 ml) and solvent removed. The resulting oil was triturated with Et_2O to give colourless needles of 4-*pyridyl N,N-dimethyldithiocarbamate* (10) (0.1 g, 25%), m.p. 102 °C (Found: N, 13.7; S, 32.9, $C_8H_{10}N_2S_2$ requires N, 14.1; S, 32.3%), $\nu_{max.}$ ($CHBr_3$) 1 570s, 1 550w, 1 498s, 1 215w, 980br, 870br, and 805s cm^{-1}; δ($CDCl_3$) 8.69 (dd, 2 H, *J* 2, 6 Hz), 7.45 (dd, 2 H, *J* 2, 6 Hz), and 3.55 (s, 6 H) (Found: *m/z* 198.0293. Calc. for $C_8H_{10}N_2S_2$: *m/z* 198.0285).

1,2,4-*Triphenylpyridinium Perchlorate* (13).—(a) 2-Carboxy-4,6-diphenylpyrylium perchlorate (11) (3.8 g, 0.01 mol) and aniline (1.8 g, 0.02 mol) were stirred in CH_2Cl_2 (40 ml) at 25 °C for 3 h. Et_2O (50 ml) was added and resulting gum was refluxed in AcOH (20 ml) for 0.5 h. Et_2O was added and the resulting white powder was filtered off; it crystallised from AcOH–Et_2O to give colourless prisms of the *pyridinium perchlorate* (13) (3.8 g, 95%) (Found: C, 67.5; H, 4.4; N, 3.4. $C_{23}H_{18}ClNO_4$ requires C, 67.7; H, 4.4; N, 3.4%), $\nu_{max.}$ ($CHBr_3$) 1 630s, 1 590s, 1 550s, and 1 080 cm^{-1}; δ[$(CD_3)_2SO$] 9.2 (d, 1 H, *J* 6 Hz), 8.6 (d, 1 H, *J* 2 Hz), 8.2 (dd, 1 H, *J* 2, 6 Hz), and 7.5 (m, 15 H).

General Methods for Preparation of 1-*Substituted* 2-*Ethoxycarbonyl*-4,6-*diphenylpyridinium Tetrafluoroborates* (15)—(18).—*Method C.* 2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (12) (0.01 mol) and amine (0.02 mol) were stirred in CH_2Cl_2 (30 ml) for the appropriate time (Table 1) at 25 °C. The solvent was removed and the residue triturated with EtOH–Et_2O to give the 2-ethoxycarbonylpyridinium tetrafluoroborate which was recrystallised from absolute EtOH. See Table 1 for physical and Tables 2 and 3 for spectral data.

Method D. As above but using NEt_3 (0.01 mol) and amine (0.01 mol). Work-up as for Method C.

1,2,4-*Triphenylpyridinium Tetrafluoroborate* (13).—2-Ethoxycarbonyl-1,4,6-triphenylpyridinium tetrafluoroborate (2 g, 0.04 mol) was refluxed in glacial AcOH (50 ml)–conc. HCl (3 ml) for 18 h. Dilution with Et_2O (100 ml) gave a white solid which was collected and recrystallised from absolute EtOH to give the pyridinium tetrafluoroborate (13) as colourless needles (1 g, 60%), which was identified by direct spectral (^1H n.m.r. and i.r.) comparison with an authentic sample prepared by the method of ref. 24.

2-*Carbamoyl*-4,6-*diphenylpyridine* (19).—A suspension of 2-ethoxycarbonyl-4,6-diphenyl-1-(2-pyridyl)pyridinium tetrafluoroborate (16) (1 g, 2 mmol) in absolute EtOH (10 ml) and ammonia (37%, 3 ml) was refluxed for 10 h. After solvent evaporation, extraction with Et_2O (50 ml) and Et_2O removal under reduced pressure (20 mmHg) gave a white solid which recrystallised from absolute EtOH to give colourless needles of the *pyridine* (19) (0.4 g, 80%), m.p. 216—218 °C (Found: C, 78.7; H, 5.2; N, 10.2. $C_{18}H_{14}N_2O$ requires C, 78.8; H, 5.1; N, 10.2%), $\nu_{max.}$ ($CHBr_3$) 3 440, 3 150, 1 695, 1 610, 1 550, 1 310, 890, and 760 cm^{-1}; δ($CDCl_3$) 8.45 (d, 1 H, *J* 2 Hz), 8.10 (d, 1 H, *J* 2 Hz), 8.08 (m, 2 H), 7.76 (m, 2 H), and 7.50 (m, 6 H).

2,4-*Diphenyl*-1-(2-*pyridyl*)*pyridinium Tetrafluoroborate* (14).—A suspension of 2-ethoxycarbonyl-4,6-diphenyl-1-(2-pyridyl)pyridinium tetrafluoroborate (16) (1 g, 0.02 mol) in absolute EtOH (10 ml) and alcoholic NaOH (5% w/w; 1 ml, 0.01 mol) was refluxed for 2 h. Et_2O (30 ml) was added and the resulting white powder filtered off and recrystallised from absolute EtOH to give the *pyridinium salt* (14) as colourless prisms (0 7 g, 80%), m.p. 153—155 °C (Found: C, 66.7; H, 4.2; N, 7.0. $C_{22}H_{17}BF_4N_2$ requires C, 66.7; H, 4 3; N, 7.0%), ($CHBr_3$) 1 630, 1 600, 1 570, 1 480, 1 470, 1 050, 900, 850, and 790 cm^{-1}; δ [$CDCl_3$–$(CD_3)_2SO$] 9.08 (d, 1 H, *J* 6 Hz), 8.58 (dd, 1 H, *J* 2, 6 Hz), 8.48 (dd, 1 H, *J* 2, 7 Hz), 8.36 (m, 2 H), 8.00 (m, 3 H), 7.78 (dd, 1 H, *J* 2, 8 Hz), and 7.70—7.34 (m, 8 H).

4,6-*Diphenyl*-1-(2-*pyridyl*)*pyridinium*-2-*carboxylate* (20).—2-Ethoxycarbonyl-4,6-diphenyl-1-(2-pyridyl)pyridinium tetrafluoroborate (14) (2.3 g, 0.05 mol) and 0.5M-NaOH (10 ml, 0.05 mol) were stirred in EtOH (10 ml) at 25 °C for 24 h. The resulting pale yellow solution was evaporated and the residue triturated with water (20 ml) to give the betaine (20) as a white solid (1 g, 80%), m.p. 130 °C (decomp.), which decomposed on attempted recrystallisation (Found: N, 7.3. $C_{23}H_{16}N_2O_2 \cdot H_2O$ requires N, 7.6%), $\nu_{max.}$ ($CHBr_3$), 3 640, 3 360, 1 650, 1 615, 1 590, 1 570, 1 550, 1 490, 1 465, 1 430, 1 325, 1 260, 990, 910, 870, 800, 770, 740, and 720 cm^{-1}; δ($CDCl_3$–CF_3CO_2H) 8.65 (d, 1 H, *J* 2.0 Hz), 8.35 (1 H, d, *J* 2.0 Hz), 7.80 (m, 6 H), and 7.60 (m, 8 H).

Decomposition of the Betaine (20) *in Alcohols.*—4,6-Diphenyl-1-(2-pyridyl)pyridinium-2-carboxylate (20) (0.05 mol) was refluxed in absolute EtOH (20 ml) for 0.5 h to give, on cooling, pale yellow prisms of 2-*ethoxy*-4,6-*diphenyl*-1-(2-*pyridyl*)-1,2-*dihydropyridine* (21) (90%), m.p. 140 °C (Found: C, 80.7; H, 6.2; N, 7.8. $C_{24}H_{22}N_2O$ requires C, 81.3; H, 6.2; N, 7.9%), $\nu_{max.}$ ($CHBr_3$) 1 640, 1 590, 1 575, 1 550, 1 490, 1 465, 1 430, 1 270, and 1 050s cm^{-1}; δ($CDCl_3$) 8.20 (dd, 1 H, *J* 2, 6 Hz), 7.30 (m, 12 H), 6.70 (m, 1 H), 6.40 (m, 2 H), 6.05 (d, 1 H, *J* 6 Hz), 4.0 (q, 2 H, *J* 7 Hz), and 1.3 (t, 3 H, *J* 7 Hz).

Refluxing in MeOH similarly gave yellow prisms of 2-*methoxy*-4,6-*diphenyl*-1-(2-*pyridyl*)-1,2-*dihydropyridine* (22) (80%), m.p. 197—199 °C (Found: C, 81.4; H, 5.4; N, 8.5. $C_{23}H_{20}N_2O$ requires C, 81.2; H, 5.9; N, 8.2%), $\nu_{max.}$ ($CHBr_3$) 1 640, 1 590, 1 490, 1 470, 1 430, 1 310d, 1 240, 1 065d, 1 000, and 980 cm^{-1}; δ($CDCl_3$) 8.20 (dd, 1 H, *J* 2, 6 Hz), 7.20 (m, 12 H), 6.7 (m, 1 H), 6.5 (m, 2 H), 6.1 (d, 1 H, *J* 6 Hz), and 3.6 (s, 3 H).

4-*Phenyl*-1-(2-*pyridyl*)*pyridinium Tetrafluoroborate* (24).—The pyridinium salt (24) (200 mg, 0.43 mmol) and t-butylamine were refluxed in ethanol (2 ml) for 24 h. The de-ethoxycarbonylated *pyridinium salt* (28) crystallised upon cooling as needles (80 mg, 60%), m.p. 188—189 °C (Found: C, 59.9; H, 4.1; N, 8.8. $C_{16}H_{13}BF_4N_2$ requires C, 60.0; H, 4.1; N, 8.7%), $\nu_{max.}$ ($CHBr_3$) 1 635, 1 615, 1 600, 1 430, and 1 045 cm^{-1}; δ[$(CD_3)_2SO$], 7.50—7.70 (m, 4 H), 8.20—8.35 (m, 4 H), 8.71 (d, 2 H *J* 6.9 Hz), 8.79 (m, 1 H), and 9.66 (d, 2 H, *J* 6.9 Hz).

Pyrimidin-2-*one* (25).—2-Ethoxycarbonyl-4,6-diphenyl-1-pyrimidin-2-ylpyridinium tetrafluoroborate (17) (3.4 g, 0.07

mol) and NaOH (0.3 g, 0.07 mol) in absolute EtOH (40 ml) were refluxed for 24 h. After solvent evaporation and washing with Et_2O, the residue was extracted into hot EtOH to give the pyrimidinone (25) contaminated with some $NaBF_4$ (0.2 g, 50%); the *picrate* crystallised from water as yellow needles, m.p. 195 °C, (Found: C, 36.8; H, 2.1; N, 21.4. $C_{10}H_7N_5O_8$ requires C, 36.9; H, 2.1; N, 21.5%), $\nu_{max.}$(CHBr$_3$) 3 300—2 500br, 1 650, 1 620, 1 550, 1 470, 1 430, 1 350, 1 300w, 990w, and 800 cm^{-1}; δ(D_2O) 8.70 (d, 2 H, *J* 6 Hz) and 6.94 (t, 1 H, *J* 6 Hz).

4,6-Dimethylpyrimidin-2-one (26) (65%) was prepared as above, m.p. 185 °C (lit.,[29] m.p. 194—196 °C); $\nu_{max.}$ (CHBr$_3$) 3 300—2 500br, 1 650, 1 630, 1 570, 1 460, 1 320, 1 030, 930, and 820 cm^{-1}; δ[$(CD_3)_2SO$] 6.70 (s, 1 H) and 2.44 (s, 6 H).

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