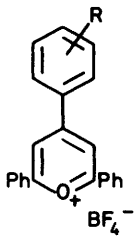
Kinetics and Mechanisms of Nucleophilic Displacements with Heterocycles as Leaving Groups. Part 4.[1] 2,4,6-Triaryl-*N*-benzylpyridinium Cations: Rate Variation with Electronic Effects in the Leaving Group

By **Alan R. Katritzky,* Jeffrey Adamson, E. Michael Elisseou, Giuseppe Musumarra, Ranjan C. Patel, Kumars Sakizadeh, and Wing Kai Yeung**, School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, Department of Chemistry, University of Florida, Gainesville, Florida, 32611 U.S.A., and Istituto Dipartimentale di Chimica e Chimica Industriale dell'Università, 95125 Catania, Italy

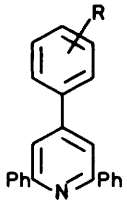
Electron-withdrawing groups in the 4-phenyl ring of 2,4,6-triphenylpyridine modestly increase its activity as a leaving group. Replacement of 2-phenyl by heteroaryl has a small effect for monoheteroaryl groups, but significantly larger for 2-benzimidazol-2-yl and especially for 2-benzothiazol-1-yl.

THE reaction of primary amines with pyrylium cations and subsequent nucleophilic displacement of the N-substituent from the resulting pyridinium cation form a two-step sequence for the conversion of primary amines into other functions of considerable synthetic significance.[2] Other work has underlined the great importance of steric acceleration by the 2- and 6-substituents in the pyridinium cation on the rate of nucleophilic displacement.[3] We now describe the preparation and kinetic study of a series of *N*-benzylpyridinium salts designed to define the significance of electronic effects in the leaving group.

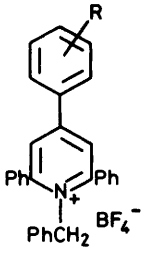
Preparation of Compounds.—A series of 4-aryl-2,6-diphenylpyrylium tetrafluoroborates (1) was prepared by the method of Reichardt and Müller:[4] reaction with ammonia and benzylamine gave, respectively, the corresponding pyridines (2) (Table 1) and 1-benzylpyridinium tetrafluoroborates (3) (Table 2).



(1)



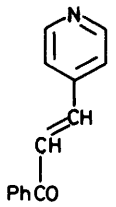
(2)



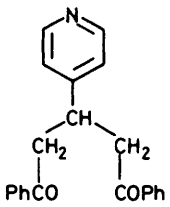
(3)

a; R = H
b; R = *p*-OMe
c; R = *p*-Me
d; R = *p*-F
e; R = *p*-Cl
f; R = *p*-Br
g; R = *m*-Cl
h; R = *m*-Br
i; R = *m*-NO_2
j; R = *p*-NO_2

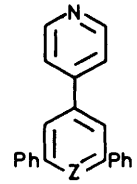
Marvel *et al.*[5] reacted pyridine-4-carbaldehyde and acetophenone to give the chalcone (4) (*ca.* 21%), but we found that this reaction in methanolic sodium methoxide gave directly the 1,5-diketone (5) (56%), which was converted by benzalacetophenone (as hydride acceptor) and boron trifluoride into the desired pyrylium salt (6). With ammonia and benzylamine, (6) gave the corresponding pyridine (7) and pyridinium salt (8). Pyrylium salt (9) was prepared by cyclisation of the methiodide of (5). The monopyridinium salt (10) was prepared by reaction of pyridine (7) with methyl iodide (tetrafluoroboric acid being used to effect the I^- to BF_4^- exchange). Methylation of the isomeric monopyridinium salt (8) gave the bispyridinium derivative (11).



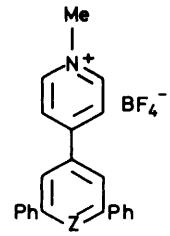
(4)



(5)



(6) Z = O^+
(7) Z = N
(8) Z = N^+CH_2Ph, BF_4^-



(9) Z = O^+
(10) Z = N
(11) Z = N^+CH_2Ph, BF_4^-

2-Methyl-4,6-diphenylpyrylium tetrafluoroborate (12) was condensed with benzaldehyde and pyridine-4-carbaldehyde to give the corresponding 4,6-diphenyl-2-styrylpyrylium (14) and 4,6-diphenyl-2-[β-(4-pyridyl)-vinyl]pyrylium (15) tetrafluoroborate. These salts were then dissolved in hot ethanol and excess of ammonia, to give respectively 4,6-diphenyl-2-styryl-(16) and 4,6-diphenyl-2-[β-(4-pyridyl)vinyl]-pyridine (17).

Similarly, condensation of benzaldehyde and pyridine-4-carbaldehyde with 1-benzyl-2-methyl-4,6-diphenylpyridinium tetrafluoroborate (13) gave respectively 1-benzyl-4,6-diphenyl-2-styryl- (19) and 1-benzyl-4,6-diphenyl-2-[β-(4-pyridyl)vinyl]-pyridinium (20) tetrafluoroborate. Compounds (17) and (20) were methylated to yield (18) and (21).

TABLE 1

Preparation of 2,6-diphenyl-4-(substituted phenyl)pyridines (2)

Starting pyrylium salt								Found (%)				Required (%)		
No.	M.p. (°C)	Lit. m.p. [a] (°C)	No.	Cryst. solvent	Cryst. form	Yield %	M.p. (°C)	C	H	N	Mol. formula	C	H	N
(1a)	253—254	253—255 [b]	(2a)	EtOH–H_2O	Needles	52	135—136 [c]	89.8	5.6	4.5	$C_{23}H_{17}N$	89.9	5.6	4.6
(1b)	253—255	251—253	(2b)	EtOH–H_2O	Plates	25	98—99	85.3	5.7	4.1	$C_{24}H_{19}NO$	85.4	5.7	4.2
(1c)	245	261—265	(2c)	EtOH	Plates	42	110	89.7	5.8	4.2	$C_{24}H_{19}N$	89.7	5.9	4.4
(1d)	210	223—224	(2d)	EtOH	Needles	20	140	85.0	4.7	4.3	$C_{23}H_{16}FN$	84.9	4.9	4.3
(1e)	255	266—273	(2e)	EtOH	Needles	56	121	81.0	4.7	3.9	$C_{23}H_{16}ClN$	80.8	4.7	4.1
(1f)	275—277	279—280	(2f)	EtOH	Needles	56	122—123	71.7	4.1	3.6	$C_{23}H_{16}BrN$	71.5	4.2	3.6
(1g)	223—226	215—219	(2g)	EtOH	Needles	51	116—117	80.8	4.8	4.1	$C_{23}H_{16}ClN$	80.8	4.7	4.1
(1h)	222—224	225—229	(2h)	EtOH	Needles	38	127—128	71.4	4.1	3.6	$C_{25}H_{16}BrN$	71.5	4.2	3.6
(1i)	270	272—276	(2i)	EtOH	Prisms	12	182—184	78.7	4.7		$C_{23}H_{16}N_2O_2$	78.4	4.6	
(1j)	268—270	279—280	(2j)	EtOH	Needles	42	130—131	78.0	4.8	7.5	$C_{23}H_{16}N_2O_2$	78.4	4.6	7.9

[a] From Ref. 4. [b] R. Lombard and J.-P. Stephan, *Bull. Soc. Chim. Fr.*, 1958, 1458. [c] Lit., m.p. 137—138 °C (W. Dilthey, *J. prakt. Chem.*, 1921, [2] **102**, 209).

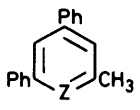
TABLE 2

Preparation of 1-benzyl-2,6-diphenyl-4-(substituted phenyl)pyridinium tetrafluoroborates (3)

No.	Cryst. solvent	Cryst. form	Yield (%)	M.p. (°C)	Found (%) C	H	N	Molecular formula	Required (%) C	H	N
(3a)	EtOH	Needles	81	195—196 [a]	74.1	5.1	3.0	$C_{30}H_{24}BF_4N$	74.2	5.0	2.9
(3b)	EtOH	Needles	41	199—200	72.5	5.1	2.8	$C_{31}H_{26}BF_4NO$	72.2	5.1	2.7
(3c)	EtOH	Needles	48	169	74.7	5.4	2.8	$C_{31}H_{26}BF_4N$	74.6	5.2	2.8
(3d)	EtOH	Needles	61	183	71.4	4.8	3.0	$C_{30}H_{23}BF_5N$	71.6	4.6	2.8
(3e)	EtOH	Needles	70	185	69.8	4.6	2.7	$C_{30}H_{23}BClF_4N$	69.3	4.5	2.7
(3f)	EtOH–Et_2O	Plates	58	118 (dec.)	63.7	4.1	2.5	$C_{30}H_{23}BBrF_4N$	63.9	4.1	2.5
(3g)	EtOH	Needles	28	122—135	67.6	4.9	2.2	$C_{30}H_{23}BClF_4N$, C_2H_5OH [b]	67.9	5.2	2.5
(3h)	EtOH–Et_2O	Needles	30	127—129	63.0	4.5	2.4	$C_{30}H_{23}BBrF_4N$, C_2H_5OH [b]	63.0	4.8	2.3
(3i)	EtOH	Needles	5	125	68.0	4.5	5.0	$C_{30}H_{23}BF_4N_2O_2$	67.9	4.4	5.3
(3j)	EtOH–Et_2O	Prisms	17	98 (dec.)	67.6	4.6	5.1	$C_{30}H_{23}BF_4N_2O_2$	67.9	4.4	5.3

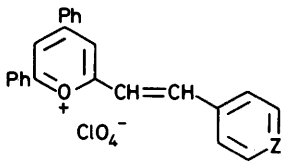
[a] Lit., m.p. 196—197 °C (A. R. Katritzky, U. Gruntz, D. H. Kenny, M. C. Rezende, and H. Sheikh, *J. Chem. Soc., Perkin Trans. 1*, 1979, 430). [b] EtOH of solvation confirmed by ^1H n.m.r.

The 2-pyridyl derivatives (22) and (23) have been described elsewhere.[6] Reaction of benzal-2-nitroacetophenone with acetophenone and perchloric acid gave 2-(2-nitrophenyl)-4,6-diphenylpyrylium perchlorate which



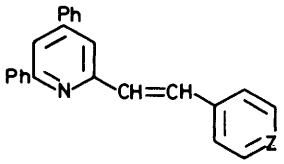
(12) Z = O^+, BF_4^-

(13) Z = N^+CH_2Ph, BF_4^-



(14) Z = CH

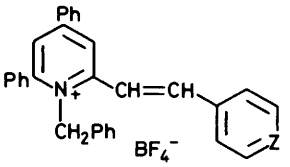
(15) Z = N



(16) Z = CH

(17) Z = N

(18) Z = N^+CH_3, BF_4^-



(19) Z = CH

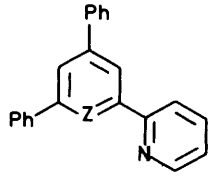
(20) Z = N

(21) Z = N^+CH_3, BF_4^-

reacted smoothly with benzylamine and ammonia to yield, respectively, (25) and (24).[7] The *N*-oxides (27) and (34) were prepared with *m*-chloroperbenzoic acid.

Kinetic Results for 1-Benzyl-2,6-diphenyl-4-(substituted phenyl)pyridiniums.—The reactions of the pyridinium salts (3) with piperidine in chlorobenzene were followed spectrophotometrically at 100 °C, by measuring the disappearance of the cation.[3,8] The 4-*p*-nitro-derivative (3j) was unstable and darkened rapidly in air: probably for this reason it did not give satisfactory kinetic results. U.v. absorption data are recorded in Table 3, and the kinetic results in Table 4. The reactions were assumed to be first-order in substrates and in piperidine (*cf.* refs. 3 and 8), and were followed under pseudo-first-order conditions at 0.16M-piperidine and 1.6×10^{-3}M-substrate to give convenient rates. Errors are not quoted in Table 4: the uncertainties for the single runs were quite small (±3%) but other systematic errors could give true errors of *ca.* ±20%.

The data in Table 4 show clearly (a) that, as expected, electron-withdrawing groups increase and electron-donor groups decrease the rate relative to the unsubstituted 4-phenyl derivatives and (b) that the effects are small. A quantitative treatment by the Hammett equation

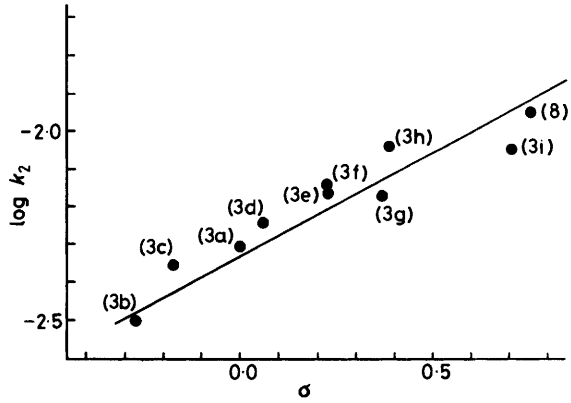


(22) Z = N

(23) Z = N^+CH_2Ph, BF_4^-

(Figure) gives a reasonable correlation (r 0.950) with ρ 0.46. The low ρ value demonstrates the intensity of the displacement reaction towards substitution in the 4-phenyl group: the reaction centre is evidently too far from the structural modification.

The rate for the 4-(4-pyridyl) compound (8) fits well into the Hammett plot. Unfortunately it was not possible to measure the bisquaternary derivative (11) due to



Hammett plot of log k_2 values for reaction of 4-aryl-1-benzyl-2,6-diphenylpyridinium cations with piperidine in chlorobenzene at 100 °C against σ values (*cf.* Table 4)

TABLE 3

U.v. spectral data for pyridinium cations (3a—i), (8), (23), (25)—(31) and the corresponding pyridines (2a—i), (7), (22), (24), (32)—(37) and extinction coefficients at the kinetic wavelength [a]

Cation	$\lambda_{max.}$/ [b]nm	ε	Pyridine	$\lambda_{max.}$/ [b]nm	ε	Kinetic wavelength (nm)	ε [c]	ε [d]
(3a)	312	34 000	(2a)	(312)	8 000	312	34 000	8 000
				253	47 000			
(3b)	360	36 635	(2b)			360	36 635	0
(3c)	327	32 740	(2c)	312	8 100	327	32 740	5 480
(3d)	314	32 650	(2d)	314	8 100	314	32 650	8 100
(3e)	318	37 100	(2e)	318	8 255	318	37 100	8 255
(3f)	320	36 260	(2f)	320	8 535	320	36 260	8 535
(3g)	303	24 765	(2g)	315	8 785	303	24 765	6 915
(3h)	304	27 100	(2h)	315	8 600	304	27 100	7 320
(3i)	292	24 670	(2i)	316	8 910	295	24 640	9 285
(8)	(321)	12 500	(7)	321	7 500	300	13 200	4 200
(23)	321	20 600	(22)	323	2 900	312	26 800 [e]	12 500 [e]
(25)	312	34 000	(24)	(305)	10 000	312	34 000	8 500
(26)	319	25 300	(33)	319	3 400	312	26 800 [e]	8 950 [e]
(27)	324	20 450	(34)	330	2 465	324	15 250 [e]	3 475 [e]
				(340)	14 950			
(28) [f]	328	27 100	(35)	328	16 510	329	29 000 [e]	20 500 [e]
	(272)	24 300		270	28 040			
	255	26 170		256	29 280			
(29)	310	28 000	(36)	308	19 900	431	13 000	1 200
	431	13 000		325	21 185			
(30)	315	28 000	(37)	327	13 400	315	28 000	11 000
				285	30 500			
(31)	315	26 000	(32)	(305)	22 400	320	25 000	11 000
				340	14 640			

[a] Solvent 2% (v/v) chlorobenzene–ethanol. [b] Shoulders in parentheses [c] Extinction coefficient of the pyridinium cation at the kinetic wavelength. [d] Extinction coefficient of the pyridine at the kinetic wavelength. [e] Solvent chlorobenzene. [f] Solvent ethanol.

TABLE 4

Second-order rate constants (k_2) [a] for the reaction of *N*-benzyl-2,6-diphenylpyridinium cations (3a—i) and (8) with piperidine in chlorobenzene at 100 °C

Compound	Hammett σ [b]	4-Substituent	[Nu]/M	$10^5 k_{obs.}$	X	$10^3 k_2$	k/k(3a)
(3a)	0	Ph			ClO_4	4.94 [c]	1
(3b)	−0.27	*p*-$MeOC_6H_4$	0.16	50.7	BF_4	3.16	0.64
(3c)	−0.17	*p*-MeC_6H_4	0.16	70.6	BF_4	4.40	0.89
(3d)	0.06	*p*-FC_6H_4	0.16	91.6	BF_4	5.70	1.15
(3e)	0.23	*p*-ClC_6H_4	0.16	111	BF_4	6.89	1.39
(3f)	0.23	*p*-BrC_6H_4	0.16	116	BF_4	7.24	1.47
(3g)	0.37	*m*-ClC_6H_4	0.16	108	BF_4	6.74	1.36
(3h)	0.39	*m*-BrC_6H_4	0.16	146	BF_4	9.15	1.85
(3i)	0.71	*m*-$O_2NC_6H_4$	0.16	145	BF_4	9.06	1.83
(8)	0.76 [d]	4-Pyridyl	0.036	41.0	BF_4	11.4	2.31
			0.054	60.0		11.2	2.27

[a] Measured under pseudo-first-order conditions, in l mol^{-1} s^{-1}. [b] From C. D. Johnson, ' The Hammett Equation,' Cambridge University Press, Cambridge, 1973, p. 3. [c] From ref. 8. [d] Footnote *b*, p. 101.

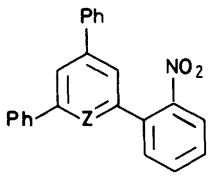
a combination of its poor solubility in chlorobenzene and of the small difference in u.v. absorption of (11) and the corresponding pyridine (10).

Kinetic Results for 1-*Benzyl*-4,6-*diphenyl*-2-(*substituted phenyl*)*pyridiniums*.—Replacement of the 2-phenyl group in (3a) by 2-*o*-nitrophenyl (25) has a modest rate increasing effect (factor of 1.8, see Table 5). Analogues of (3a) in which the 2-phenyl group is replaced by a heteroaryl with a single heteroatom are similarly slightly more active: 2-(2-thienyl) (30), 2-(3-pyridyl) (23), and 2-(2-pyridyl) (26) show factors of 1.7, 2.3, and 3.6, respectively, and the bis-2-thienyl analogue (31) a factor of 4.0.

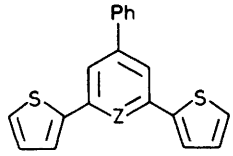
However, replacement of the 2-phenyl group in (3a) by a heteroaryl containing two heteroatoms has considerably greater impact: for the 2-benzimidazol-2-yl (29) and the 2-benzothiazol-2-yl (28) compounds the factors are 9 and 64. The latter compound (28) reacted too rapidly at 100 °C for convenient measurement, and the data in Table 5 were obtained by a temperature extrapolation from those data of Table 6. A plot of log k against $1/T$ gave $\Delta H_{373}^{\ddagger}$ 20.3 ± 2.8 kcal mol^{-1} and $\Delta S_{373}^{\ddagger}$ −6.9 ± 8.9 cal mol^{-1} K^{-1}. The latter figure is less negative than expected for an S_N2 reaction [9] but the experimental uncertainty is large.

The large effect of the 2-benzothiazol-2-yl substituent is clearly an electronic effect, as sterically it is unlikely to be very different from a 2-phenyl group.

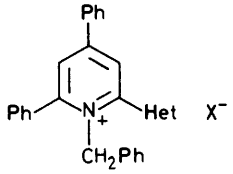
The 2-styryl derivative (19) and heteroanalogues (20) and (21) did not give clean kinetics with piperidine, probably due to Michael addition of the nucleophile across the C=C bond. We also attempted to assess their activity as alkylating agents kinetically with dimethyl-



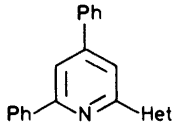
(24) Z = N
(25) Z = N^+CH_2Ph, ClO_4^-



(31) Z = N^+CH_2Ph, ClO_4^-
(32) Z = N



(26) Het = 3-pyridyl, X = ClO_4
(27) Het = *N*-oxido-2-pyridyl, X = CF_3SO_3
(28) Het = benzothiazol-2-yl, X = ClO_4
(29) Het = benzimidazol-2-yl, X = ClO_4
(30) Het = 2-thienyl, X = ClO_4



(33) Het = 3-pyridyl
(34) Het = *N*-oxido-2-pyridyl
(35) Het = benzothiazol-2-yl
(36) Het = benzimidazol-2-yl
(37) Het = 2-thienyl

thiourea as nucleophile,[10] but clean kinetics were not again obtained.

Conclusions.—Electron-withdrawing groups substituted into the 4-phenyl group of 2,4,6-triphenylpyridine do increase its activity as a leaving group, but only by a very small factor. The same appears to apply also to variation of the 2-phenyl group as far as the *o*-nitro or monoaza substitution is concerned. However, significant and interesting enhancement of rate is found for 2-benzimidazol-2-yl and especially 2-benzothiazol-2-yl.

EXPERIMENTAL

I.r. and n.m.r. spectra were measured with Perkin-Elmer 237 and R12 (60 MHz) and Varian HA100 (100 MHz) instruments respectively. U.v. spectra of reactants and products were run on a Pye–Unicam SP 800A spectrophotometer. For the rate measurements at fixed wavelength, u.v. spectrophotometers of type Pye–Unicam SP 8-200 (temperature programmable) and Pye–Unicam SP 6-500 were used. Stoppered glass tubes (28 cm height and 13.5 mm diameter) were used as reaction vessels which were placed into the hot-blocks (Statim Model PROP.) for convenient temperature runs. M.p.s (uncorrected) were determined on a Reichert hot-stage apparatus.

Preparation of Compounds.—The preparation of the following compounds has been reported in the references quoted: (a) 4,6-diphenyl-2-(2-pyridyl)pyridine (22) and 1-benzyl-4,6-diphenyl-2-(2-pyridyl)pyridinium tetrafluoroborate (23) in ref. 6; (b) 2-(2-nitrophenyl)-4,6-diphenylpyridine (24) and 1-benzyl-2-(2-nitrophenyl)-4,6-diphenylpyridinium perchlorate (25) in ref. 7; (c) 4,6-diphenyl-2-(3-pyridyl)pyridine (33) and 1-benzyl-4,6-diphenyl-2-(3-pyridyl)pyridinium perchlorate (26) in ref. 6; (d) benzothiazol-2-yl- (35), benzimidazol-2-yl- (36), and 2-thienyl- (37) 4,6-diphenylpyridines, 4-phenyl-2,6-dithienylpyridine (32), benzothiazol-2-yl- (28), benzimidazol-2-yl- (29), and 2-thienyl- (30) 1-benzyl-4,6-diphenylpyridinium perchlorates, and 1-benzyl-4-phenyl-2,6-dithienylpyridinium perchlorate (31) in ref. 11.

4-*Aryl*-2,6-*diphenylpyrylium Tetrafluoroborates* (1a—j).—The substituted aldehyde (1 mol) and acetophenone (2 mol) were heated together with boron trifluoride–diethyl ether (40%, 3 mol) for 2 h at 100 °C. The hot reaction mixture was then poured into rapidly stirred Et_2O to give yellow crystals of the pyrylium tetrafluoroborate, which was recrystallised from absolute EtOH (Table 1).

TABLE 5

Second-order rate constants (k_2) [a] for the reactions of *N*-benzyl-4-phenyl-2,6-disubstituted pyridinium cations with piperidine in chlorobenzene at 100 °C

Cation	R^2	R^6	X	$10^2 k_2$	k/k(3a)
(3a)	Ph	Ph	ClO_4	0.494 [b]	1
(23)	2-Pyridyl	Ph	BF_4	1.80 [c]	3.6
(25)	*o*-$O_2NC_6H_4$	Ph	ClO_4	0.882 [d]	1.8
(26)	3-Pyridyl	Ph	ClO_4	1.12 [e]	2.3
(27)	*N*-Oxido-2-pyridyl	Ph	CF_3SO_3	0.67 [f]	1.4
(28)	Benzothiazol-2-yl	Ph	ClO_4	31.6 [g]	64
(29)	Benzimidazol-2-yl	Ph	ClO_4 [h]	4.35 [i]	9
(30)	2-Thienyl	Ph	ClO_4	0.819 [d]	1.7
(31)	2-Thienyl	2-Thienyl	ClO_4	1.99 [d]	4.0

[a] Measured under pseudo-first-order conditions, in 1 mol^{-1} s^{-1}. [b] From ref. 8. [c] Average value between two k_2 values calculated by dividing pseudo-first-order rate constants by piperidine concentration. 10^5 $k_{obs.}/s^{-1}$, [piperidine]/M 3.00, 0.0016; 5.50, 0.0032. Pyridinium concentration 3.2×10^{-5}M. [d] Calculated by dividing pseudo-first-order rate constant by piperidine concentration (equal to 0.16M). [e] ±0.29 (90% confidence limit) k_2 value calculated from the plot of $k_{obs.}$ *versus* piperidine concentration. 10^5 $k_{obs.}/s^{-1}$ [piperidine] (M): 2.70, 0.0016; 4.70, 0.0032; 8.10, 0.0064. Pyridinium concentration 3.2×10^{-5}M. [f] Average value between two k_2 values calculated by dividing pseudo-first-order rate constants by piperidine concentration. 10^5 $k_{obs.}/s^{-1}$, [piperidine]/M 3.10, 0.0032; 6.40, 0.008 06. Pyridinium concentration 2.8×10^{-5}M. [g] Extrapolated value from Table 6. [h] Although bisperchlorate was used, the monocation is almost certainly the reactive species. [i] ±0.41 (90% confidence limit); k_2 value calculated from the plot of $k_{obs.}$ *versus* piperidine concentration. 10^5 $k_{obs.}/s^{-1}$, [piperidine]/M 64.0, 0.016; 13.3, 0.032; 210, 0.048; 270, 0.064. Pyridinium concentration 3.2×10^{-5}M.

TABLE 6

Observed ($k_{obs.}$) and second-order (k_2) rate constants for the reaction of (28) with piperidine in chlorobenzene

	T (°C)					
	34.5	39.5	44.5	50	60	[Piperidine] [a]/M
$10^5 k_{obs.}$/s^{-1}	0.6	5.6	10.8	12.8	11.2	0.032
	2.6	8.9		13.8	34.6	0.0576
	3.9	10.7	21.4	25.3		0.08
		15.8			84.2	0.102
				41.4		0.134
		24.6	41.8	61.6		0.160
$10^3 k_2$ [b]/l mol^{-1} s^{-1}	0.689	1.50	2.43	3.77	10.4	
	±0.363	±0.23	±0.57	±1.24	±3.1	

[a] Concentration of (28) 3.2×10^{-5}M. [b] 90% Confidence limit.

4-Aryl-2,6-diphenylpyridines (2a—j).—The appropriate pyrylium tetrafluoroborate was heated in EtOH. To this hot suspension, excess of aqueous ammonia (35%) was added. On cooling, a precipitate was deposited; it crystallised from EtOH or EtOH–H_2O to give the pyridine (Table 1).

4-Aryl-1-benzyl-2,6-diphenylpyridinium Tetrafluoroborates (3a—j).—The appropriate 4-aryl-2,6-diphenylpyrylium tetrafluoroborate (1 mol) and benzylamine (1.2 mol) were stirred in EtOH for 12 h at 25 °C. The resulting crystals of the 1-benzylpyridinium salt were recrystallised (Table 2).

1,5-Diphenyl-3-(4-pyridyl)pentane-1,5-dione (5).—Sodium hydride (0.15 g, 0.006 mol) was added to MeOH (15 ml) at 0 °C. Acetophenone was then added and the mixture stirred vigorously. Pyridine-4-carbaldehyde (2 g, 0.019 mol) was added slowly, maintaining the temperature at 0—10 °C. Water was added dropwise until a milky suspension was obtained. After 4 h stirring, a brown viscous oil settled. The mixture was left at 0 °C for 12 h. The resulting solid was crystallised from aqueous EtOH (90%) to give fluffy needles of the *dione* (1.12 g, 56%), m.p. 126—128 °C (lit.,[5] 125—126 °C) (Found: C, 80.0; H, 5.7; N, 4.1. $C_{22}H_{19}NO_2$ requires C, 80.2; H, 5.8; N, 4.2%); $\nu_{max.}$ (Nujol) 1 685 (s), 1 600 (s), 1 580 (v), 1 235 (w-m), 1 415 (m), 995 (m), 880 (w-m), 750 (s), and 685 (s) cm^{-1}; δ (100 MHz, $CDCl_3$) 3.40 (4 H, d), 4.00 (1 H, q), 7.35—7.90 (13 H, m), and 8.5br (1 H, s).

2,6-Diphenyl-4-[(1H)-pyridinium-4-yl]pyrylium Bistetrafluoroborate (6).—1,5-Diphenyl-3-(4-pyridyl)pentane-1,5-dione (5.0 g, 0.015 mol) and benzalacetophenone (3.3 g, 0.016 mol) were dissolved in hot glacial acetic acid (8 ml). Boron trifluoride–diethyl ether (40%, 20 ml) was added dropwise. The resulting red solution was refluxed for 12 h. After cooling and stirring with Et_2O (50 ml) the resulting orange crystals of the *pyrylium bistetrafluoroborate* were collected and recrystallised from CH_3CO_2H to give orange rosettes (6.0 g, 81%), m.p. 275—277 °C (Found: C, 54.7; H, 3.8; N, 3.2. $C_{22}H_{17}B_2F_8NO$ requires C, 54.4; H, 3.5; N, 2.9%); $\nu_{max.}$ ($CHBr_3$) 1 630 (vs), 1 620 (s), 1 610 (s), 1 600 (s), 1 590 (s), 1 570 (s), 1 540 (vs), 1 510 (s), 1 460 (s), 1 430 (s), and 1 060 (br) cm^{-1}; δ (100 MHz, $CDCl_3$–CF_3CO_2H) 7.05—9.15 (m).

2,6-Diphenyl-4-(4-pyridyl)pyridine (7).—2,6-Diphenyl-4-[(1*H*)-pyridinium-4-yl]pyrylium bistetrafluoroborate (4.0 g, 0.008 mol) in absolute EtOH (8 ml) was stirred with excess of aqueous ammonia (80%, 1.82 ml, 0.033 mol) for 12 h. The resulting crystals were collected and recrystallised from absolute EtOH to the *pyridine* as needles (1.6 g, 63%), m.p. 188—189 and 230 °C (Found: C, 84.8; H, 5.0; N, 8.9. $C_{22}H_{16}N_2$,0.25H_2O requires C, 84.5; H, 5.3; N, 9.0%); $\nu_{max.}$ ($CHBr_3$) 3 350 (br), 1 590 (vs), 1 580 (vs), 1 565 (s), 1 535 (s), 1 495 (s), and 1 400 (s) cm^{-1}; δ (100 MHz, $CDCl_3$–CF_3CO_2H) 7.20—8.70 (m).

1-Benzyl-2,6-diphenyl-4-(4-pyridyl)pyridinium Tetrafluoroborate (8).—2,6-Diphenyl-4-[(1*H*)-pyridinium-4-yl]pyrylium bistetrafluoroborate (2.05 g, 4.23 mmol) and benzylamine (0.9 ml, 8.46 mmol) were refluxed in glacial acetic acid (10 ml) for 12 h. The resulting crystalline deposit of the *1-benzylpyridinium salt* was collected and recrystallised from absolute EtOH to give prisms, (1.5 g, 73%), m.p. 120—121 °C (Found: C, 70.9; H, 4.8; N, 5.4. $C_{29}H_{23}BF_4N_2$,0.25H_2O requires C, 70.9; H, 4.8; N, 5.7%); $\nu_{max.}$ ($CHBr_3$) 3 400 (br), 1 630 (s), 1 595 (s), 1 570 (m), 1 545 (m), 1 490 (m), 1 400 (s), and 1 050 (br) cm^{-1}; δ (100 MHz, $CDCl_3$–CF_3CO_2H) 5.79 (2 H, s), 6.45—7.20 (5 H, m), and 7.50—8.95 (16 H, m).

3-(1-Methylpyridinium-4-yl)-1,5-diphenylpentane-1,5-dione Iodide.—MeI (2.2 g, 0.0152 mol) was added to 1,5-diphenyl-3-(4-pyridyl)pentane-1,5-dione (5.0 g, 0.0152 mol) dissolved in $CHCl_3$ (6 ml). The mixture was stirred at 20 °C for 0.5 h. The $CHCl_3$ was evaporated at 20 mmHg and the light green oil that remained was triturated with Et_2O. The *3-(1-methylpyridinium-4-yl)-1,5-diphenylpentane-1,5-dione iodide* precipitated as crystals which were crystallised from EtOH, rosettes (6.5 g, 91%), m.p. 179—181 °C (Found: C, 58.7; H, 4.7; N, 2.7. $C_{23}H_{22}INO_2$ requires C, 58.6; H, 4.7; N, 3.0%); $\nu_{max.}$ ($CHBr_3$) 1 680 (s), 1 640 (s), 1 600 (s), 1 580 (m), 1 450 (s), 1 360 (m), and 1 275 (w) cm^{-1}; δ (60 MHz, $CDCl_3$–CF_3CO_2H) 2.28 (1 H, m), 3.80 (4 H, d), 4.35 (3 H, s), and 7.30—8.70 (14 H, m).

4-(1-Methylpyridinium-4-yl)-2,6-diphenylpyrylium Bistetrafluoroborate (9).—3-(1-Methylpyridinium-4-yl)-1,5-diphenylpentane-1,5-dione iodide (3 g, 0.006 mol) was dissolved with benzalacetophenone (1.4 g, 0.007 mol) in hot glacial acetic acid (8 ml). Boron trifluoride–diethyl ether (excess, 20 ml) was added to the refluxing mixture. Heating was maintained for 12 h. The thick mass was dissolved in hot acetic acid (10 ml) and poured into stirred Et_2O. The resulting orange crystals were recrystallised from glacial acetic acid to give the *pyrylium bistetrafluoroborate* as orange rosettes (2.4 g, 76%), m.p. 240 and 269—272 °C (Found: C, 53.7; H, 3.7; N, 2.8. $C_{23}H_{19}B_2F_8NO$,-H_2O requires C, 53.4; H, 4.1; N, 2.7%); $\nu_{max.}$ ($CHBr_3$) 3 300 (br), 1 630 (vs), 1 600 (w), 1 580 (m), 1 510 (m), 1 460 (s), 1 430 (s), and 1 050 (br) cm^{-1}; δ (100 MHz, $CDCl_3$–CF_3CO_2H) 4.45 (3 H, s) and 7.19—9.10 (m).

4-(1-Methylpyridinium-4-yl)-2,6-diphenylpyridine Tetrafluoroborate (10).—To 2,6-diphenyl-4-(4-pyridyl)pyridine (0.5 g, 0.002 mol) dissolved in $CHCl_3$ (5 ml) was added MeI (0.23 g, 0.002 mol). The mixture was stirred at 25 °C for 0.5 h. The solvent was removed *in vacuo* (20 mmHg) and the residue triturated with aqueous tetrafluoroboric acid (40%, 2 ml) and Et_2O (25 ml). The pale yellow crystals were filtered off and dried to give the *tetrafluoroborate salt* (10) which crystallised from absolute EtOH as pale yellow

needles (0.62 g, 93%), m.p. 225—227 and 260—262 °C (Found: C, 66.5; H, 4.5; N, 7.3. $C_{23}H_{19}BF_4N_2,0.25H_2O$ requires C, 66.6; H, 4.7; N, 6.8%); $\nu_{max.}$ ($CHBr_3$) 3 500 (br), 3 240 (s), 3 140 (shoulder), 1 640 (s), 1 595 (s), 1 555 (s), 1 505 (m), 1 405 (s), 1 050 (br), and 800 (vs) cm^{-1}; δ (100 MHz, $CDCl_3$) 4.30 (3 H, s) and 7.40—9.25 (16 H, m).

1-*Benzyl*-4-(1-*methylpyridinium*-4-*yl*)-2,6-*diphenylpyridinium Bistetrafluoroborate* (11).—1-Benzyl-2,6-diphenyl-4-(4-pyridyl)pyridinium tetrafluoroborate (0.63 g, 1.3 mmol) and MeI (0.2 g, 3.9 mmol) were stirred in glacial acetic acid (8 ml) for 6 h. Excess of tetrafluoroboric acid was added and the mixture triturated with Et_2O (50 ml). The resulting yellow crystals of the *bistetrafluoroborate* salt were recrystallised from acetic acid to give yellow rosettes (0.55 g, 72%), m.p. 156—158 °C (Found: C, 60.4; H, 4.2; N, 4.8. $C_{30}H_{26}B_2F_8N_2,0.5H_2O$ requires C, 60.3; H, 4.5; N, 4.7%); $\nu_{max.}$ ($CHBr_3$) 3 350 (br), 1 630 (s), 1 600 (w), 1 570 (m), 1 515 (w), 1 495 (m), 1 455 (m), 1 425 (m), 1 050 (br), and 755 (m) cm^{-1}; δ (100 MHz, $CDCl_3$–CF_3CO_2H) 4.27 (3 H, s), 5.78 (2 H, s), 6.50—7.20 (3 H, m), and 7.30—8.80 (18 H, m).

1-*Benzyl*-2-*methyl*-4,6-*diphenylpyridinium Tetrafluoroborate* (13).—This was prepared following the standard procedure described above for the 4-aryl-2,6-diphenylpyridinium tetrafluoroborates (62%), m.p. 229—231 °C (lit.,[12] 227—229 °C).

4,6-*Diphenyl*-2-*styrylpyridine* (16).—To 4,6-diphenyl-2-styrylpyrylium perchlorate [13] (0.45 g, 1.03 mmol) dissolved in hot EtOH (8 ml) was added an excess of ammonia solution (35%, 10 ml). After heating for 5 min, the dark brown mixture was poured over ice (5 g). Vigorous trituration of the cooled mixture gave the *pyridine* as brown rosettes crystallised from EtOH (0.31 g, 90%), m.p. 103—105 °C (Found: C, 88.7; H, 5.9. $C_{25}H_{19}N,0.25H_2O$ requires C, 88.9; H, 5.8%); $\nu_{max.}$ ($CHBr_3$) 3 400 (br), 1 595 (s), 1 580 (shoulder), 1 545 (s), 1 495 (s), 1 450 (s), 760 (s), and 690 (s) cm^{-1}; δ (60 MHz, $CDCl_3$) 6.40—8.30 (19 H, m).

4,6-*Diphenyl*-2-[β-(4-*pyridyl*)*vinyl*]*pyridine* (17).—This was prepared as above from 4,6-diphenyl-2-[β-(4-pyridyl)-vinyl]pyrylium tetrafluoroborate (0.45 g, 1.06 mmol) and excess of ammonia (35%, 10 ml). It separated from ethanol as dark purple *rosettes* (0.2 g, 20%), m.p. 136—138 °C (Found: C, 86.2; H, 5.4. $C_{24}H_{18}N_2$ requires C, 85.9; H, 5.3%); $\nu_{max.}$ ($CHBr_3$) 1 600 (s), 1 580 (shoulder), 1 550 (m), 1 515 (m), 1 515 (w), 1 495 (s), 1 450 (s), 1 415 (s), and 760 (s) cm^{-1}; δ (100 MHz, $CDCl_3$) 3.71 (1 H, d), 4.55 (1 H, d), and 6.50—8.50 (16 H, m).

2-[β-(1-*Methylpyridinium*-4-*yl*)*vinyl*]-4,6-*diphenylpyridine Tetrafluoroborate* (18).—4,6-Diphenyl-2-[β-(4-pyridyl)-vinyl]pyridine (0.25 g, 0.75 mmol) and MeI (0.3 g, 2.24 (mmol) were stirred in $CHCl_3$ (10 ml) for 0.5 h. After solvent removal *in vacuo* (20 mmHg) excess of tetrafluoroboric acid (40%, 1 ml) was added to the residue and the mixture triturated with Et_2O (40 ml). The resulting dark brown material was crystallised from EtOH–Et_2O (1 : 3) to give purple microcrystals of the *pyridine tetrafluoroborate* (0.3 g, 92%), m.p. 195—197 °C (Found: C, 68.5; H, 4.8. $C_{25}H_{21}BF_4N_2$ requires C, 68.8; H, 4.8%); $\nu_{max.}$ ($CHBr_3$) 1 640 (s), 1 620 (s), 1 595 (s), 1 580 (m), 1 050 (br), 760 (s), 720 (s), and 690 (s) cm^{-1}; δ (100 MHz, $CDCl_3$–CF_3CO_2H) 4.20 (3 H, s) and 6.90—8.40 (22 H, m).

1-*Benzyl*-4,6-*diphenyl*-2-*styrylpyridinium Tetrafluoroborate* (19).—To 1-benzyl-2-methyl-4,6-diphenylpyridinium tetrafluoroborate (1.0 g, 0.0024 mol) in hot EtOH (5 ml) with piperidine (0.12 ml, 0.0012 mol), was added benzaldehyde (0.26 g, 0.0024 mol). After 0.5 h reflux, the green mixture was cooled to give green rosettes, recrystallised from EtOH, of the *styrylpyridinium tetrafluoroborate* (1.08 g, 87%), m.p. 185 °C (Found: C, 74.0; H, 5.1; N, 3.1. $C_{32}H_{26}BF_4N,0.5H_2O$ requires C, 73.8; H, 5.2; N, 2.7%); $\nu_{max.}$ ($CHBr_3$) 3 400 (br), 1 630 (s), 1 620 (s), 1 600 (m), 1 585 (w), 1 575 (w), 1 565 (w), 1 555 (s), 1 500(s), 1 455 (s), 1 1415 (m), and 1 055 (br) cm^{-1}; δ (60 MHz, $CDCl_3$–CF_3CO_2-H) 5.77 (2 H, d) and 7.00—8.38 (24 H, m).

1-*Benzyl*-4,6-*diphenyl*-2-[β-(4-*pyridyl*)*vinyl*]*pyridinium Tetrafluoroborate* (20).—1-Benzyl-2-methyl-4,6-diphenylpyridinium tetrafluoroborate (1.0 g, 0.0024 mol) was refluxed in EtOH (5 ml) with piperidine (0.12 ml, 0.0012 mol) for 5 min. Pyridine-4-carbaldehyde (0.26 g, 0.0024 mol) was then added to the refluxing solution. After 0.5 h reflux, the mauve mixture was cooled; the separated product was crystallised from EtOH to give the *pyridinium tetrafluoroborate* as ivory rosettes (1.07 g, 86%), m.p. 170—171 °C (Found: C, 71.0; H, 4.7; N, 4.8. $C_{31}H_{25}BF_4N_2,-0.5H_2O$ requires C, 71.4; H, 5.0; N, 5.3%); $\nu_{max.}$ ($CHBr_3$) 3 490 (br), 1 630 (m), 1 615 (vs), 1 590 (s), 1 560 (w), 1 555 (m), and 1 050 (br) cm^{-1}; δ (60 MHz, $CDCl_3$–CF_3CO_2H) 5.80 (2 H, d) and 7.90—9.10 (23 H, m).

1-*Benzyl*-2-[β-(1-*methylpyridinium*-4-*yl*)*vinyl*]-4,6-*diphenylpyridinium Bistetrafluoroborate* (21).—1-Benzyl-4,6-diphenyl-2-(4-pyridyl)pyridinium tetrafluoroborate (0.2 g, 0.4 mmol) was stirred in $CHCl_3$ (5 ml) with MeI (0.06 g, 0.4 mmol) for 0.5 h. After solvent removal (20 mmHg), Et_2O was added to the residue followed by tetrafluoroboric acid (0.1 g). The solution was triturated with ether and the resulting crystals were filtered off and recrystallised from EtOH to give the *bistetrafluoroborate* as microcrystals (0.2 g, 81%), m.p. 170 °C (Found: C, 62.9; H, 4.2; N, 4.6. $C_{32}H_{28}B_2F_8N_2$ requires C, 62.5; H, 4.5; N, 4.6%); $\nu_{max.}$ ($CHBr_3$) 1 620 (vs), 1 600 (s), 1 560 (m), 1 495 (w), 1 425 (w), 1 060 (br), and 765 (m) cm^{-1}; δ (100 MHz, $CDCl_3$–CF_3CO_2H) 4.41 (3 H, s), 5.82 (2 H, s), 6.85—7.17 (5 H, m), and 7.45—8.50 (18 H, m).

1-*Benzyl*-4,6-*diphenyl*-2-(N-*oxido*-2-*pyridyl*)*pyridinium Trifluoromethanesulphonate* (27).—1-Benzyl-4,6-diphenyl-2-(2-pyridyl)pyridinium trifluoromethane sulphonate (0.66 g, 1.21 mmol) and *m*-chloroperbenzoic acid (0.31 g, 1.81 mmol) were stirred in $CHCl_3$ (5 ml) for 3 days. The mixture was shaken successively with sodium sulphite (10%, 25 ml) and $NaHCO_3$ (5%, 25 ml). The aqueous layer was separated and washed with $CHCl_3$ (15 ml), in each successive step. The organic layer was dried over $MgSO_4$ and filtered. Removal of the $CHCl_3$ afforded light brown *plates* (0.48 g, 71%), m.p. 75—80 °C (Found: C, 64.0; H, 3.8; N, 4.9. $C_{30}H_{23}F_3N_2O_4S$ requires C, 63.8; H, 4.1; N, 5.0%); $\nu_{max.}$ ($CHBr_3$) 1 620 (vs), 1 604 (s), 1 600 (w-m, shoulder), 1 568 (s), 1 560 (w-m, shoulder), 1 492 (s), 1 455 (m), 1 420 (s), 1 265 (s, br), and 1 026 (vs) cm^{-1}; δ [60 MHz, $(CD_3)_2SO$] 5.70 (2 H, s), 6.80—8.50 (20 H, m), and 8.80 (1 H, d).

4,6-*Diphenyl*-2-(N-*oxido*-2-*pyridyl*)*pyridine* (34).—4,6-Diphenyl-2-(2-pyridyl)pyridine (22) (0.58 g, 1.90 mmol) and *m*-chloroperbenzoic acid (0.50 g, 2.93 mmol) were stirred in CH_2Cl_2 (5 ml) for 2 days. A solid (*m*-chlorobenzoic acid) precipitated out of solution. This was filtered off and the filtrate washed with aqueous sodium sulphite (10%, 25 ml). The mixture was then transferred to a separating funnel and the organic layer washed with aqueous $NaHCO_3$ (5%, 25 ml). The combined aqueous layers were shaken with CH_2Cl_2 (30 ml). All the organic layers were combined, washed with distilled H_2O (15 ml), and dried over $MgSO_4$. Removal of the CH_2Cl_2 gave the N-*oxide* (34) (0.39 g, 64%) which was

analysed as the *picrate* (yellow microcrystals from EtOH), m.p. 227—232 °C (Found: C, 60.4; H, 3.4; N, 12.4. $C_{28}H_{19}N_5O_8$ requires C, 60.8; H, 3.4; N, 12.7%); $\nu_{max.}$ ($CHBr_3$) 1 610 (w-m), 1 590 (vs), 1 579 (s), 1 545 (vs), 1 492 (s), 1 485 (s), 1 450 (m), 1 430 (m-s), 1 396 (vs), 1 275 (w), 1 245 (w-m), 1 025 (w-m), 860 (m), and 759 (vs) cm^{-1}; δ (60 MHz, $CDCl_3$) 7.25—8.52 (15 H, m) and 9.24 (1 H, d).

Kinetic Measurements.—Kinetics were followed by u.v. spectrophotometry monitoring the decrease of absorbance of pyridinium cation at a fixed wavelength, using the procedure already described.[8] In typical runs under pseudo-first-order conditions the concentration of pyridinium was 1.6×10^{-3} mol l^{-1}, while those of the nucleophile varied from 0.0016 to 0.16 mol l^{-1}. Pseudo-first-order rate constants were calculated from the slope of $\ln[a/(a - x)] = \ln[(\varepsilon_1 - \varepsilon_2)/(\varepsilon - \varepsilon_2)]$ *versus* time. These plots were linear to at least 85% completion. Second-order rate constants were calculated by dividing pseudo-first-order rates by nucleophile concentration. The kinetic wavelength and the extinction coefficients at that wavelength in 2% (v/v) chlorobenzene–ethanol are reported in Table 3.

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