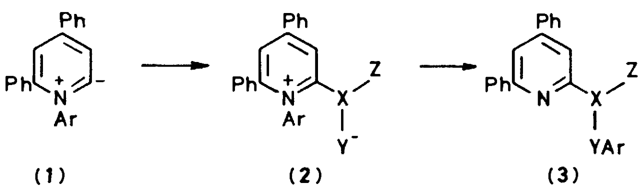
Some Novel Reactions of Pyridinium-2-carboxylate Betaines[1]

Alan R. Katritzky,* Andrew J. Cozens, Andrea Ossana, Olga Rubio, and (in part) Nadira Dabbas
Department of Chemistry, University of Florida, Gainesville, Florida 32611, USA

Appropriate 2-ethoxycarbonylpyridinium salts are hydrolysed to 1-aryl-4,6-diphenylpyridinium-2-carboxylate betaines which undergo thermal decarboxylation to afford, in the presence of acids, 1-aryl-2,4-diphenylpyridinium salts. The intermediate ylides are captured by acid chlorides to yield 2-acylpyridinium salts and by CS_2 to give dithio analogues of the starting betaines. With bromine, the carboxylate betaine yields a 2,2′-bipyridyl bisquaternary salt.

1-Benzyl-4,6-diphenylpyridinium-2-carboxylate with benzoyl chloride yields 2-benzoyl-4,6-diphenylpyridine and benzyl chloride. Benzaldehydes in place of PhCOCl, also gave 2-acylpyridines.

The original objective of the present work was to induce aryl migration in intermediates of type (2), related to previously studied intramolecular nucleophilic attacks on *N*-aryl groups in suitably substituted pyridinium salts which resulted in easy displacement at the *ipso*-carbon atom of the *N*-aryl group, and transfer to an oxygen,[2] sulphur,[3] or nitrogen[1,4] atom.



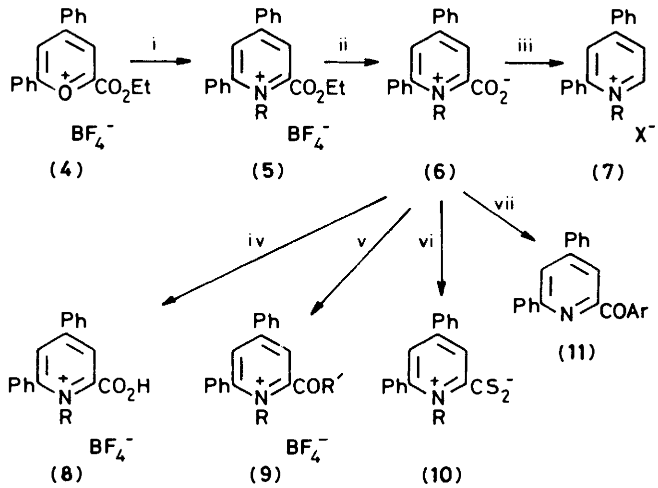
Scheme 1.

While rearrangements (2)→(3) were not achieved, several new reactions of the zwitterions (1) were disclosed. Transformations of type (1)→(2) have been reported by several authors, notably Ratts[5] (capture by RCHO) and Quast[6,7] (capture by diazonium salts and by azides), and we now considerably extend the range of this reaction type.

2-Ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate (4)[8] reacted with aniline, *p*-toluidine, and benzylamine under standard conditions[8,9] to give the corresponding 1-substituted pyridinium salts (**5a**—**c**) in high yields. These pyridinium-2-esters (**5a**—**c**) were hydrolysed by aqueous sodium hydroxide at ambient temperature[9] to the 1-substituted 4,6-diphenylpyridinium-2-carboxylate betaines (**6a**—**c**) in good yield. The crystalline carboxylate betaines (**6a**) and (**6b**) contain water of crystallisation, as shown by a singlet (2H) in their ^1H n.m.r. spectra at δ 2.9, and by elemental analysis.[9] Anhydrous samples could not be obtained; both drying over magnesium sulphate in methylene chloride and attempted recrystallisation caused decomposition.

1-Aryl-4,6-diphenylpyridinium-2-carboxylates (**6a**) and (**6b**) were converted into the 2-carboxy salts (**8a**) and (**8b**) in methylene chloride at 0 °C with tetrafluoroboric acid. The acid tetrafluoroborates were obtained analytically pure, free of water of crystallisation and in good yield. Their i.r. spectra showed the appearance of the BF_4^- band at 1 050 cm^{-1} and a shift of the carbonyl stretching band from 1 650 cm^{-1} in (**6a**) and (**6b**) to 1 720 cm^{-1} in (**8a**) and (**8b**).

Decarboxylation of the 1-*Substituted* 4,6-*Diphenylpyridinium*-2-*carboxylates* (**6a**—**c**).—The 2-carboxy salts (**8a**) and (**8b**) are thermally unstable. When recrystallised from ethanol, the C=O band at 1 720 cm^{-1} was lost from the i.r. spectra, and elemental analysis confirmed loss of CO_2.



(**5**)—(**10**): **a**, R = Ph; **b**, R = 4-MeC_6H_4; **c**, R = CH_2Ph
(**7**): **A**, X = I; **B**, X = Br; **C**, X = Cl
(**9**): **A**, R′ = Ph; R′ = Me
(**11**): **a**, Ar = Ph; **b**, Ar = *p*-MeC_6H_4; **c**, Ar = *p*-$NO_2C_6H_4$; **d**, Ar = *p*-ClC_6H_4

Scheme 2. *Reagents:* i, RNH_2; ii, NaOH–H_2O; iii, HX; iv, HBF_4; v, R′COCl; vi, CS_2; vii, PhCOCl or ArCHO

1,4,6-Triphenylpyridinium-2-carboxylate (**6a**) was previously[9] decarboxylated by heating in THF in the presence of HI to yield 1,2,4-triphenylpyridinium iodide. We have now generalised this reaction with other halogenoacids to provide a convenient synthesis of the 1-substituted 2,4-diphenylpyridinium iodide, chloride, and bromide salts (**7aA**—**7aC**) (Table 1). The ^1H n.m.r. spectra of salts (**7**) show the expected characteristic signals[9] (Table 2): a doublet at *ca.* δ 9.3 (J_o 7 Hz) due to the 6-H, a double doublet at *ca.* δ 8.7 (J_o 7 Hz, J_m 2 Hz) due to 5-H, and a doublet at δ 8.7—8.2 (J_m 2 Hz) due to 3-H. The i.r. spectra notably show the loss of the carbonyl stretching band at 1 650 cm^{-1} characteristic of the 2-carboxylates (**6a**) and (**6b**).

When heated at 85 °C in an excess of benzoyl chloride or at reflux in acetyl chloride, the 1-arylpyridinium-2-carboxylates (**6**) form the corresponding 1-aryl-2-acyl-4,6-diphenylpyridinium chlorides. These hygroscopic chlorides were converted into the analogous tetrafluoroborates (**9**) with tetrafluoroboric acid in ethanol (Table 1). (However, phenylacetyl chloride with (**6b**) gave only 1-(*p*-tolyl)-2,4-diphenylpyridinium tetrafluoroborate after work-up of the crude product with tetrafluoroboric acid.) The ^1H n.m.r. spectra of the 2-acylpyridinium salts show the 3-H and 5-H ring protons as doublets (*J* 2 Hz) at

Table 1. Preparation of 1-arylpyridinium salts (7)—(9)

Product	1-Substituent	R′[a]	Anion	Yield (%)	M.p.[b] (°C)	Found (%) (Required) C	H	N	Formula
(7aA)	Ph		I	95	272[c]	63.4 (63.5)	4.0 (4.1)	3.2 (3.2)	$C_{23}H_{18}IN$
(7bA)	4-MeC_6H_4		I	90	211	63.6 (64.1)	4.2 (4.5)	2.9 (3.1)	$C_{24}H_{20}IN$
(7aB)	Ph		Br	84	261—263	71.5 (71.1)	4.6 (4.7)	3.5 (3.6)	$C_{23}H_{18}BrN$
(7bB)	4-MeC_6H_4		Br	81	221—225	71.4 (71.6)	5.3 (5.0)	3.5 (3.5)	$C_{24}H_{20}BrN$
(7aC)	Ph		Cl	65	265	79.9 (80.3)	5.1 (5.3)	4.1 (4.1)	$C_{23}H_{18}ClN$
(8a)	Ph		BF_4	85	185—188[d]	65.4 (65.6)	4.2 (4.1)	3.1 (3.2)	$C_{24}H_{18}BF_4NO_2$
(8b)	4-MeC_6H_4		BF_4	62	156—158 (decomp.)[d]	66.4 (66.3)	4.7 (4.5)	3.3 (3.1)	$C_{25}H_{20}BF_4NO_2$
(9aA)	Ph	Ph	BF_4	82	276—278	72.0 (72.2)	4.6 (4.4)	2.4 (2.8)	$C_{30}H_{22}BF_4NO$
(9aB)	Ph	Me	BF_4	73	262—264	68.6 (68.7)	4.4 (4.6)	3.1 (3.2)	$C_{25}H_{20}BF_4NO$
(9bA)	4-MeC_6H_4	Ph	BF_4	75	265	72.2 (72.5)	4.5 (4.7)	2.8 (2.7)	$C_{31}H_{24}BF_4NO$
(9bB)	4-MeC_6H_4	Me	BF_4	68	293	68.9 (69.2)	5.0 (4.9)	3.1 (3.1)	$C_{26}H_{22}BF_4NO$

[a] R′ refers to compounds (9). [b] Needles from absolute EtOH. [c] Lit.,[9] m.p. 273—274 °C. [d] Microcrystals, crude material, too labile to be recrystallised.

Table 2. ^1H N.m.r. spectra[a] of 1-aryl-2,4-diphenylpyridinium halides (7aA—7aC)

Compd. No.	1-Substituent	Anion	6-CH (1 H, d, J_o 7)	5-CH (1 H, dd, J_o7, J_m 2)	3-CH (1 H, d, J_m 2)	Ar-H m	H	Me (3 H, s)
(7aA)	Ph	I	9.25	8.65	8.25	7.6—7.1	15	
(7bA)	4-MeC_6H_4	I	9.20	8.55	8.25	7.5—7.0	14	2.20
(7aB)	Ph	Br	9.43	8.90	8.64	7.9—7.2	15	
(7bB)	4-MeC_6H_4	Br	9.45	8.80	8.75	8.3—7.1	14	2.20
(7aC)	Ph	Cl	9.25	8.60	8.20	7.6—7.1	15	

[a] Solutions in $CDCl_3$; δ in p.p.m., J = coupling constant in Hz.

Table 3. ^1H N.m.r. spectra[a] of 2-substituted 1-aryl-4,6-diphenylpyridinium salts (8)—(9)

Compd. No.	1-Substituent	R′[b]	3-CH (1 H, d, J 2)	5-CH (1 H, d, J 2)	Ar-H (m)	H	COMe (3 H, s)	Me (3 H, s)
(8a)	Ph	OH	8.75[c]	8.43[c]	8.3—7.2	15		
(8b)	4-MeC_6H_4	OH	8.20	8.02	8.0—6.7	14		2.15
(9aA)	Ph	Ph	8.25	8.25	7.6—7.2	20		
(9aB)	Ph	Me	8.25	8.00	7.7—7.4	15	2.28	
(9bA)	4-MeC_6H_4	Ph	8.35	8.20	8.0—7.0	19		2.20
(9bB)	4-MeC_6H_4	Me	8.15	8.00	7.9—6.9	14	2.28	2.20

[a] Solutions in $CDCl_3$ except (8a) in $CDCl_3$–CF_3CO_2H; δ in p.p.m.; J = coupling constants in Hz. [b] R′ refers to formula (9). [c] Distorted signal.

ca. δ 8.3 and 8.1; for (**9aB**) and (**9bB**) the COMe singlets resonate at δ 2.3 (Table 3). The i.r. spectra show a carbonyl absorption at 1 680 cm^{-1} for (**9aA**) and (**9bA**) and at 1 710 cm^{-1} for (**9aB**) and (**9bB**). Attempts to deprotonate and rearrange (**9aB**) failed.

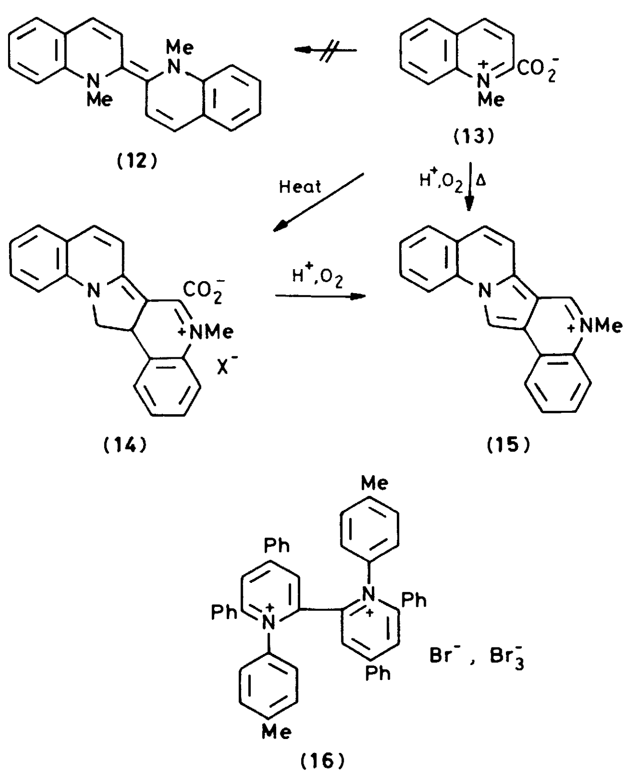
1-Aryl-4,6-diphenylpyridinium-2-dithiocarboxylates (**10a**) and (**10b**) were obtained by refluxing the appropriate pyridinium-2-carboxylate in carbon disulphide for 6 days. Strong bands at 1 520 cm^{-1} are observed in the i.r. spectra of (**10a**) and (**10b**). Attempts to induce migration of the *N*-aryl group to sulphur failed: on heating (**10a**) at 150 °C in the atmosphere, the product showed the i.r. spectrum of (**6a**) (carbonyl stretching at 1 650 cm^{-1}), probably by trapping atmospheric CO_2 *via* the ylide (**1**). The betaine (**10a**) was unchanged by heating at 150 °C in a sealed tube.

Heating the 1-arylpyridinium-2-carboxylates (**6a**) and (**6b**) in the presence of phenyl isothiocyanate, or 2-chlorobenzaldehyde, or acetic anhydride, at reflux in THF or at 80 °C without solvent, followed by acidic work-up, gave only the 1-aryl-2,4-diphenylpyridinium salts (**7**). In some cases the proton source may have been the water of crystallisation contained in (**6**) (see above).

We have also studied decarboxylative dimerisation of the betaines. In 1966, Scheutzow[10] reported that 1-methylquinolinium-2-carboxylate (**13**) when heated gave the dimer

(12). Later, Quast[11] showed that the product was actually the dimeric betaine (14) which readily formed (15). In our betaine, such a reaction at the *N*-substituent is unlikely and simple dimerisation is likely to occur: indeed dimeric products were formed on heating the 2-carboxy salts (8), but together with varying amounts of simple decarboxylation. Reproducible dimer formation was accomplished by reaction of the carboxy betaine (6b) with bromine, which gave the mixed bromide–tribromide (16).

1-Benzyl-4,6-diphenylpyridinium-2-carboxylate (6c) was converted by benzoyl chloride at 80 °C into 2-benzoyl-4,6-diphenylpyridine (11a): the expected addition to the 2-position of the pyridinium ring had thus occurred, and the 1-benzyl group was eliminated in the form of benzyl chloride. The 2-carboxylate (6c) with benzaldehyde, 4-methylbenzaldehyde, 4-nitrobenzaldehyde, or 4-chlorobenzaldehyde in each case gave the corresponding 2-acylpyridine (11a—d) when heated either neat at 80 °C or in refluxing methylene chloride (Table 4). In these reactions the 1-benzyl group was also lost, however, and attempts to isolate the second product(s) were unsuccessful. Neither toluene nor dibenzyl ether could be detected in the reaction mixture. The ^{1}H n.m.r. spectra of the pyridines (11a—d) show multiplets in the aromatic region (Table 4). In their i.r. spectra the carbonyl group absorbs at 1 680 cm^{-1}. The lack of the characteristic pyridinium ring absorption at 1 620 cm^{-1} and the strong absorption at 1 600 cm^{-1} support the pyridine structure.



Attempts to prepare Compounds capable of generating a Stabilized Carbanion of Type (2; Y = CRR′).—We reasoned that pyridinium salts with a 2-substituent of the type CH=CHX might form a zwitterion Py^+·CR=C^-–X, if X were a suitably activating group. Alternatively, a 2-substituent of type C(Me)=CRX could lose a proton from the Me group to form a zwitterion of type (2). Attempts designed along these lines are now described.

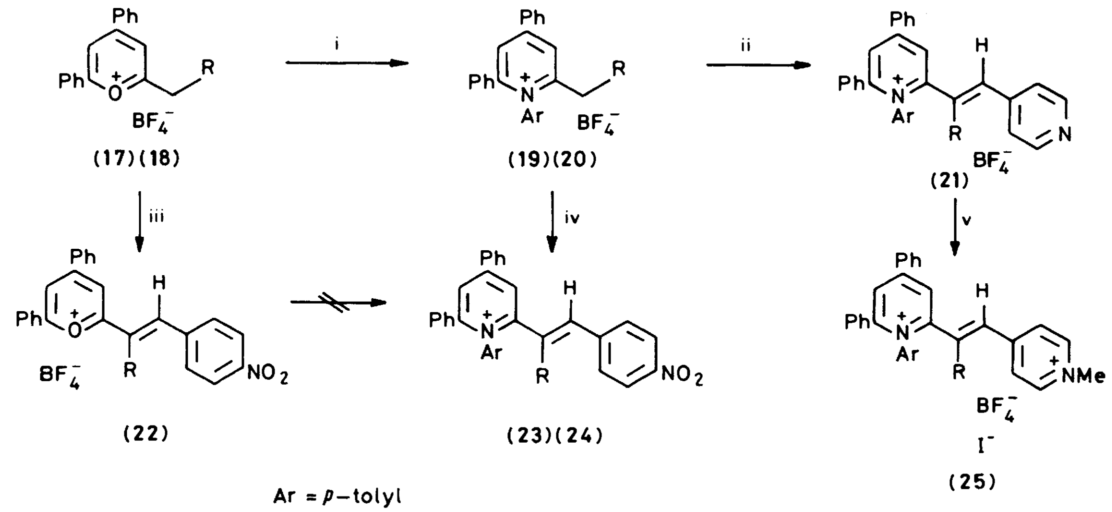
2-Methyl-4,6-diphenylpyrylium tetrafluoroborate (17) (from acetophenone and acetic anhydride[12]) with 4-methylaniline gave the corresponding 1-(*p*-tolyl)pyridinium salt (19). Salt (19) was condensed with 4-nitrobenzaldehyde and with pyridine-4-carbaldehyde in ethanol, using piperidine as base, to give 1-(*p*-tolyl)-2-(4-nitrostyryl)-4,6-diphenylpyridinium tetrafluoroborate (23) (85%), and the corresponding 2-[2-(4-pyridyl)vinyl] derivative (21), respectively. The ^{1}H n.m.r. spectrum of (23) shows the methyl group at δ 2.3, the β-vinyl proton at δ 6.9 as a doublet (*J* 16 Hz), the 3-H pyridinium ring proton at δ 8.6 as a doublet (*J* 2 Hz), and the remaining protons as a multiplet (20 H) at δ 7.2—8.2. In (21) both olefinic protons are hidden under the aromatic multiplet (δ 7.3—8.25, 22 H); the methyl singlet is observed at δ 2.3. The 2-[2-(4-pyridyl)vinyl]pyridinium salt (21) was converted by methyl iodide into the quarternary salt (25) (87%). Attempts to deprotonate these compounds (21), (23), and (25) led to no recognizable products of rearrangement.

The pyrylium salts (22) and (29) were prepared from the corresponding 2-ethylpyrylium (18) and tetrahydrochromenylium salts (28) by condensation with 4-nitrobenzaldehyde.[13] Treating the pyrylium salt (22) with *p*-toluidine under various conditions (CH_2Cl_2–TFA–AcOH,[14] refluxing ethanol, refluxing acetic acid,[15] and in benzene–ethanol under Dean-Stark conditions[16]) gave a mixture of the desired (24) and the retro-aldol product (20) in a 70:30 ratio, as identified by ^{1}H and ^{13}C n.m.r. spectroscopy. Column chromatography (silica gel, ethyl acetate–1% acetic acid, 2% capacity) gave only (20) identified by ^{1}H n.m.r. Presumably, a retro-aldol condensation of (24) to give (20) occurred on the column. Attempted reaction of (29) with *p*-toluidine, and of the pyridinium salt (20) or the 1-(*p*-

Table 4. Reaction of 1-benzyl-4,6-diphenylpyridinium-2-carboxylate (6c) with benzaldehydes and benzoyl chloride

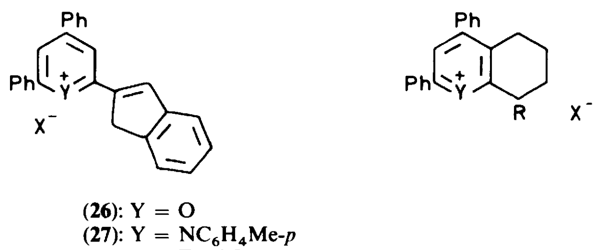
Electrophile	Product	Yield (%)	Temp. (°C)	M.p.[a] (°C)	Found (%) (Required) C	H	N	Formula	^{1}H n.m.r.[b]
PhCHO	(11a)	70	80	123	86.0 (86.0)	5.0 (5.1)	4.1 (4.1)	$C_{24}H_{17}NO$	8.4—8.0 (6 H, m), 8.0—7.5 (11 H, m)
PhCOCl	(11a)	60	80	122	86.0 (86.0)	5.0 (5.1)	4.1 (4.1)	$C_{24}H_{17}NO$	
4-MeC$_6$H$_4$CHO[c]	(11b)	75	80	130	85.9 (86.0)	4.0 (4.0)	5.3 (5.3)	$C_{25}H_{19}NO$	8.1—7.6 (6 H, m), 7.6—6.6 (10 H, m)
4-NO$_2$C$_6$H$_4$CHO[d]	(11c)	80	40	120	75.5 (75.5)	4.2 (4.2)	7.2 (7.2)	$C_{24}H_{16}N_2O_3$	8.7—8.5 (4 H, m), 8.5—7.3 (12 H, m)
4-ClC$_6$H$_4$CHO[d]	(11d)	85	40	128	77.8 (77.9)	3.7 (3.8)	4.3 (4.3)	$C_{24}H_{16}ClNO$	8.3—7.9 (6 H, m), 7.9—7.3 (10 H, m)

[a] All needles except (11b) prisms. [b] Solutions in $CDCl_3$; δ in p.p.m.; *J* = coupling constant in Hz. [c] 2.22 (3 H, s, Me). [d] Reaction carried out in CH_2Cl_2 solution.



(17), (19), (21), (23), (25): R = H
(18), (20), (22), (24): R = Me

Scheme 3. *Reagents:* i, 4-$MeC_6H_4NH_2$; ii, *p*-$CHOC_5H_4N$, $C_5H_{11}N$; iii, *p*-$NO_2C_6H_4CHO$; iv, *p*-$NO_2C_6H_4CHO$, $C_5H_{11}N$; v, MeI.



(26): Y = O
(27): Y = NC_6H_4Me-*p*
a, X = F_3CSO_3
b, X = BF_4

(28): Y = O, R = H
(29): Y = O, R = =$CHC_6H_4NO_2$-*p*
(30): Y = NC_6H_4-4-Br, R = H
(31): Y = NC_6H_4-4-Br, R = =$CHC_6H_4NO_2$-*p*

bromophenyl)-2,4-diphenyl-5,6,7,8-tetrahydroquinolinium salt **(30)** with 4-nitrobenzaldehyde, failed.

The pyrylium salt **(26)** was prepared from 2-acetylindene (*i*) by reaction of 2 equiv. of 1,3-diphenylpropenone with trifluoromethanesulphonic acid in ether and (*ii*) by using 1 equiv. of the chalcone and triphenylmethane tetrafluoroborate as hydride abstractor. The former route gave the desired **(26a)** in 7% yield, whereas the latter gave crude **(26b)** (30%); this could not be purified. Reaction of the pyrylium salts **(26)** with *p*-toluidine to give the pyridinium salts appeared to occur as was shown by the ^1H n.m.r. spectrum by a singlet at δ 2.35, an upfield shift of the two methylene protons by 1.05 p.p.m. as compared to the pyrylium salt and a doublet at δ 8.42 due to the 5-H proton. However, compounds **(27a,b)** could not be purified.

Experimental

M.p.s (uncorrected) were taken on a hot-stage microscope. ^1H n.m.r. spectra were recorded with a Varian EM 360L spectrometer in $CDCl_3$ with $SiMe_4$ as an internal standard. The i.r. spectra were obtained with a Perkin-Elmer 283B spectrophotometer as Nujol mulls in $CHBr_3$. Mass spectra were recorded on an AEI MS 30 spectrometer.

The following compounds were prepared by the literature methods quoted: 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate **(4)**, m.p. 153—155 °C (lit.,[8] 155—157 °C); 2-methyl-4,6-diphenylpyrylium tetrafluoroborate **(17)**, m.p. 235—240 °C (lit.,[12] 248—249 °C); 1-phenyl- **(5a)**, m.p. 184—186 °C (lit.,[9] 185—186 °C), 1-(*p*-tolyl)- **(5b)**, m.p. 202—203 °C (lit.,[4] 202—203 °C), and 1-benzyl-2-ethoxycarbonyl-4,6-diphenylpyridinium tetrafluoroborate **(5c)**, m.p. 168—170 °C (lit.,[8] 172—174 °C); 1-phenyl- **(6a)**, m.p. 150—151 °C (lit.,[9] 150 °C), 1-(*p*-tolyl)- **(6b)**, m.p. 162—163 °C (lit.,[4] 162—163 °C), and 1-benzyl-4,6-diphenylpyridinium-2-carboxylate **(6c)**, m.p. 131—132 °C (lit.,[8] 131—132 °C); 2-ethyl-4,6-diphenylpyrylium tetrafluoroborate **(18)**, m.p. 260—262 °C (lit.,[12] 261—262 °C); 2,4-diphenyl-5,6,7,8-tetrahydrochromenylium trifluoromethanesulphonate **(28)**, m.p. 181—182 °C (lit.,[17] 187 °C); 1-(*p*-bromophenyl)-2,4-diphenyl-5,6,7,8-tetrahydroquinolinium trifluoromethanesulphonate **(30)**, m.p. 158—161 °C (lit.,[1] 158—159 °C); 2-acetylindene, m.p. 56—58 °C (lit.,[18] m.p. 59—60 °C).

Preparation of 1-Aryl-2-carboxy-4,6-diphenylpyridinium Tetrafluoroborates **(8a,b)**.—1,4,6-Triphenylpyridinium-2-carboxylate **(6a)** (0.9 g, 2.5 mmol) was dissolved in CH_2Cl_2 (10 ml); HBF_4 (40%, 1 ml) was added at 0 °C and the whole stirred at 0 °C for 0.5 h. The solution was then extracted into CH_2Cl_2 (2 × 10 ml), dried ($MgSO_4$), and concentrated (25 °C/25 mmHg). Precipitation with Et_2O gave the *2-carboxy salt* **(8a)** (0.9 g, 85%). Compound **(8b)** was similarly prepared (see Table 1).

General Method for the Preparation of 1-Aryl-2,4-diphenylpyridinium Halides **(7aA—7aC)**.—The appropriate 1-aryl-4,6-diphenylpyridinium-2-carboxylate **(6)** (5.7 mmol) was refluxed with aqueous HI (65%, 1.20 g, 6.1 mmol), HCl (36—38%, 0.65 g, 6.1 mmol) or HBr (40%, 1.23 g, 6.1 mmol) in THF (50 ml) for 4 h. After cooling, the solution was concentrated (25 °C/25 mmHg) and the residue triturated with ether to yield the products (65—95%) (Tables 1 and 2).

General Method for the Preparation of 1-Aryl-2-acyl-4,6-diphenylpyridinium Tetrafluoroborates **(9aA—9bB)**.—The pyridinium betaine **(6)** (2.5 mmol) was heated at 85 °C for 4 h with benzoyl chloride (5 ml) and then at reflux (52 °C) with acetyl chloride (5 ml) (protected by a $CaCl_2$ drying tube). On cooling the solution was poured into ether (100 ml) and the resulting solid collected. The tetrafluoroborate salts were obtained by dissolving the crude chlorides in EtOH (5 ml) and adding HBF_4 (40%, 1 ml), followed by trituration with ether, filtration, and recrystallisation from absolute EtOH (Tables 1 and 3).

Preparation of 1-Aryl-4,6-diphenylpyridinium-2-dithiocarboxylates (**10a,b**).—1,4,6-Triphenylpyridinium-2-carboxylate (**6a**) (1 g, 2.85 mmol) and CS_2 (10 ml) were refluxed for 6 days. The resulting dark brown solution was evaporated (25 °C/25 mmHg) and the residue washed with ether to give the *dithiocarboxylate* (**10a**) (0.7 g, 65%), m.p. 142 °C, δ($CDCl_3$) 9.28 (1 H, br d), 8.67 (1 H, br d), 8.4—8.0 (2 H, m), and 7.9—7.2 (13 H, m) (Found: C, 74.8; H, 4.3; N, 3.5. $C_{24}H_{17}NS_2$ requires C, 75.2; H, 4.5; N, 3.7%).

4,6-Diphenyl-1-(p-tolyl)pyridinium-2-dithiocarboxylate (**10b**).—This was similarly prepared (70%), m.p. 158 °C: δ($CDCl_3$) 9.20 (1 H, br d), 8.62 (1 H, br d), 8.2—7.9 (2 H, m), 7.8—7.2 (12 H, m), and 2.3 (3 H, s) (Found: C, 75.7; H, 4.4; N, 3.4. $C_{25}H_{19}NS_2$ requires C, 75.6; H, 4.8; N, 3.5%).

Reaction of 1-Benzyl-4,6-diphenylpyridinium-2-carboxylate (**6c**) *with Electrophiles.—Method A: with benzoyl chloride.* The pyridinium betaine (**6c**) (0.91 g, 2.5 mmol) and benzoyl chloride (5 ml) were heated at 80 °C for 4 h. After cooling to room temperature, water (20 ml) was added, and the reaction mixture was stirred for 72 h. Extraction with CH_2Cl_2 (2 × 25 ml), washing of the organic layer with saturated aqueous $NaHCO_3$ (150 ml), drying ($MgSO_4$), removal of the solvent under reduced pressure (40 °C/20 mmHg), and trituration of the residue with EtOH gave 2-benzoyl-4,6-diphenylpyridine (**11a**) (Table 4). After removal of the EtOH (40 °C/20 mmHg) from the filtrate, the oily residue was distilled in a Kugelrohr apparatus (150 °C/25 mmHg) to give benzyl chloride; δ($CDCl_3$) 4.62 (2 H, s) and 7.52 (5 H, m) (*cf.* ref. 19); *m/z* 126 (M^+, 23.8%) and 91 (100%).

Method B. The pyridinium betaine (**6c**) (2.5 mmol) and the benzaldehyde (5 ml) were heated at 80 °C for 4 h. After cooling, trituration with EtOH gave 2-benzoyl-4,6-diphenylpyridines (**11a**) and (**11b**) (Table 4).

Method C. The pyridinium betaine (**6c**) (2.5 mmol) and the substituted benzaldehyde (12.5 mmol) in CH_2Cl_2 (15 ml) were refluxed for 16 h. After cooling, the solvent was removed (40 °C/20 mmHg), and the residue precipitated with EtOH to give the 2-benzoyl-4,6-diphenylpyridines (**11c**) and (**11d**) (Table 4).

4,4′,6,6′-Tetraphenyl-1,1′-di-p-tolyl-2,2′-bipyridinium Salt (**16**). The betaine (**6b**) (1 g, 2.7 mmol) was added to a solution of bromine (1.6 g, 10 mmol) in $CHCl_3$ (45 ml) and heated to reflux immediately. After 30 min the solvent was evaporated, and the crystalline residue was filtered and washed with ether to yield the *title compound* (**16**) (1 g, 77%), m.p. 175—180 °C (decomp.); δ($CDCl_3$–TFA) 2.37 (3 H, s), 7.30 (5 H, s), 7.6—7.4 (4 H, m), 7.9—7.7 (3 H, m), 8.1—8.0 (2 H, m), 8.45 (1 H, d, *J* 2 Hz), and 8.80 (1 H, d, *J* 2 Hz) (Found: C, 60.8; H, 3.6; N, 2.8; Br, 29.3. $C_{48}H_{38}Br_4N_2$ requires C, 59.9; H, 3.9; N, 2.9; Br, 33.3%).

2-Methyl-4,6-diphenyl-1-(p-tolyl)pyridinium Tetrafluoroborate (**19**).—*p*-Toluidine (1.92 g, 18 mmol) was added to a stirred suspension of 2-methyl-4,6-diphenylpyrylium tetrafluoroborate (**17**) (3 g, 9 mmol) in absolute EtOH (40 ml) and the mixture was refluxed for 6 h. On cooling to 25 °C the *product* (**19**) separated; it crystallised from absolute EtOH as needles (3.2 g, 85%), m.p. 224—227 °C (Found: C, 70.7; H, 5.3; N, 3.3. $C_{25}H_{22}BF_4N$ requires C, 71.0; H, 5.2; N, 3.3%).

2-(p-Nitrostyryl)-4,6-diphenyl-1-(p-tolyl)pyridinium Tetrafluoroborate (**23**).—2-Methyl-4,6-diphenyl-1-(*p*-tolyl)pyridinium tetrafluoroborate (**19**) (2 g, 4.7 mmol), absolute EtOH (5 ml), 4-nitrobenzaldehyde (0.76 g, 5 mmol), and piperidine (0.4 g, 4.7 mmol) were refluxed for 2 h. The *pyridinium salt* separated and was filtered off, washed with ether (50 ml), and crystallised from absolute EtOH to give green needles (2.2 g, 84%), m.p. 253 °C; δ($CDCl_3$–TFA) 2.38 (3 H, s), 6.70 (1 H, d, *J* 16 Hz), and 7.1—8.6 (21 H, m) (Found: C, 69.4; H, 4.4; N, 4.8. $C_{32}H_{25}BF_4N_2O_2$ requires C, 69.1; H, 4.5; N, 5.0%).

2-[2-(4-Pyridyl)vinyl]-4,6-diphenyl-1-(p-tolyl)pyridinium Tetrafluoroborate (**21**).—To 2-methyl-4,6-diphenyl-1-*p*-tolylpyridinium tetrafluoroborate (**19**) (2 g, 4.7 mmol) in absolute EtOH (5 ml) were added pyridine-4-carbaldehyde (0.54 g, 5 mmol) and piperidine (0.40 g, 4.7 mmol). The mixture was refluxed for 4 h. The separated *tetrafluoroborate* was filtered off, washed with ether (50 ml), and crystallised from absolute EtOH to give needles (2.0 g, 83%), m.p. 215 °C; δ($CDCl_3$–TFA) 2.30 (3 H, s) and 7.0—8.7 (22 H, s) (Found: C, 72.3; H, 4.8; N, 5.2. $C_{31}H_{25}BF_4N_2$ requires C, 72.7; H, 4.9; N, 5.5%).

2-[2-(1-Methyl-4-pyridinio)vinyl]-4,6-diphenyl-1-(p-tolyl)pyridinium Tetrafluoroborate Iodide (**25**).—2-[2-(4-Pyridyl)vinyl]-4,6-diphenyl-1-*p*-tolylpyridinium tetrafluoroborate (**21**) (2 g, 3.9 mmol), CH_2Cl_2 (20 ml), and methyl iodide (1.7 g, 12 mmol) were stirred at 25 °C for 6 h. The *iodide* separated after addition of ether (30 ml), forming orange needles (2.2 g, 86%), m.p. 274 °C; δ($CDCl_3$–TFA) 2.30 (3 H, s), 4.26 (3 H, s), and 7.0—8.6 (22 H, m) (Found: C, 58.3; H, 4.4; N, 4.2. $C_{32}H_{28}BF_4IN_2$ requires C, 58.7; H, 4.3; N, 4.3%).

2-[1-(p-Nitrophenyl)propen-2-yl]-4,6-diphenylpyrylium Tetrafluoroborate (**22**).—2-Ethyl-4,6-diphenylpyrylium tetrafluoroborate (3.5 g, 10 mmol) and 4-nitrobenzaldehyde (2.27 g, 15 mmol) were refluxed in acetic acid (30 ml) for 2 h, whereupon a yellow solid precipitated. The mixture was filtered whilst hot and the product washed with acetic acid and ether to yield (**22**) as orange *needles* (4.4 g, 91%), m.p. 276—278 °C; δ($CDCl_3$–TFA), 2.60 (3 H, s), 7.8—8.1 (8 H, m), and 8.2—8.8 (9 H, m) (Found: C, 64.8; H, 4.3; N, 2.8; $C_{26}H_{20}BF_4NO_3$ requires C, 64.9; H, 4.2; N, 2.9%).

2-Ethyl-4,6-diphenyl-1-(p-tolyl)pyridinium Tetrafluoroborate (**20**).—*p*-Toluidine (3.7 g, 34 mmol) in ethanol (10 ml) was added to 2-ethyl-4,6-diphenylpyrylium tetrafluoroborate (6 g, 17.2 mmol) in ethanol (70 ml), and the mixture refluxed for 6 h. After 16 h at 0 °C the crystals were filtered off, washed with ether, and recrystallised from acetic acid to give (**20**) as colourless prisms (6.8 g, 90%), m.p. 185—188 °C; δ($CDCl_3$–TFA) 1.37 (3 H, t, *J* 7 Hz), 2.42 (3 H, s), 2.90 (2 H, q, *J* 7 Hz), 7.1—7.5 (10 H, m) and 7.7—8.4 (6 H, m) (Found: C, 71.1; H, 5.7; N, 3.1. $C_{26}H_{24}BF_4N$ requires C, 71.4; H, 5.5; N, 3.2%).

5,6,7,8-Tetrahydro-8-(p-nitrophenylmethylene)-2,4-diphenylchromenylium Trifluoromethanesulphonate (**29**).—5,6,7,8-Tetrahydro-2,4-diphenylchromenylium trifluoromethanesulphonate (2 g, 4.6 mmol) and 4-nitrobenzaldehyde (1.2 g, 7.7 mmol) in acetic acid (18 ml) were refluxed for 4 h. Upon cooling the product was precipitated with ether to yield (**29**) (2 g, 77%) as orange plates, m.p. 243—246 °C; δ($CDCl_3$–TFA) 1.8—2.3 (2 H, m), 3.0—3.3 (4 H, m), 7.7—8.1 (10 H, m), and 8.3—8.7 (6 H, m) (Found: C, 61.2; H, 3.9; N, 2.3; $C_{29}H_{22}F_3NO_6S$ requires C, 61.2; H, 3.9; N, 2.5%).

2-Inden-2-yl-4,6-diphenylpyrylium Trifluoromethanesulphonate (**26a**).—2-Acetylindene (1 g, 5.6 mmol), 1,3-diphenylpropenone (2.45 g, 11.8 mmol) and trifluoromethanesulphonic acid (0.48 g, 5.6 mmol) were stirred in ether (10 ml) for 16 h. The resulting dark mixture was diluted with ether (20 ml) and the crystals filtered off to yield (**26a**) (200 mg, 7%) as dark red (fluorescent) needles, m.p. 265—270 °C; δ($CDCl_3$–TFA) 4.20 (2 H, d, *J* 2 Hz) and 7.5—8.7 (17 H, m) (Found: C, 64.6; H, 3.9. $C_{27}H_{19}F_3O_4S$ requires C, 65.3; H, 3.8%).

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