Preparation and Reactions of Pyrylium Salts containing α-Pyridyl Groups [1]

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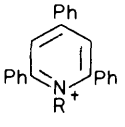
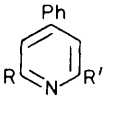
The preparation of unsymmetrical 2,4,6-trisubstituted pyrylium salts from αβ-unsaturated ketones and methyl ketones is complicated by retro-aldol reactions leading to corresponding symmetrical pyrylium salts.

4,6-Diphenyl-2-(1*H*-pyridinium-2-yl)pyrylium (5a) and (5b) is prepared successfully by oxidation of the 1,5-dione from chalcone and 2-acetylpyridine. The transformation of pyrylium into pyridinium occurs easily with primary amines to 2-(2-pyridyl)pyridiniums whose various reactions are studied.

We have shown [2] that *N*-alkyl groups in 1-substituted-2,4,6-triphenylpyridinium salts (1) are susceptible to nucleophilic attack, with displacement of 2,4,6-triphenylpyridine (2a). The original objective of the present work was to investigate intramolecular analogues of this reaction. We planned to prepare pyrylium salts containing α-functionalised substituents, use these to convert amines into the corresponding pyridinium salts, and to study the reactions of the latter. Our initial work centred on the replacement of a phenyl group of (2a) by a pyridyl group *cf.* (2b). The only pyridyl substituted pyrylium salt previously reported is the 2,6-dimethyl-4-(2-pyridyl) derivative prepared from 2,6-dimethyl-4-pyrone and 2-lithiopyridyl.[3]



(1)



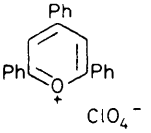
(2)

a; R = R′ = Ph
b; R = Ph, R′ = 2-py
c; R = R′ = 2-py
d; R = Bu^t, R′ = 3-py

The Preparation of 2-Pyridylpyrylium Salts.—Attempted preparation of 2,4-diphenyl-6-(2-pyridyl)-pyrylium perchlorate from 2-acetylpyridine and chalcone in the presence of perchloric acid gave only 2-acetylpyridinium perchlorate (18%) and 2,4,6-triphenylpyrylium perchlorate (3) (11%), the latter evidently from retro-aldolisation of chalcone.

Precedents for such retro-aldolisations are known: although 2-mesityl-4,6-diphenylpyrylium perchlorate could not be obtained from 2,4,6-trimethylacetophenone and chalcone, it did result from mesityl styryl ketone and acetophenone.[4] 2-Pyridyl styryl ketone,[5] however reacted with acetophenone and boron trifluoride–diethyl ether to give a mixture of the 4-phenyl-2,6-di-(2-pyridyl) (4a) and 4,6-diphenyl-2-(2-pyridyl) (4b) salts. This was shown by treating the product with ammonia to give a mixture of the symmetrical terpyridyl (2c) and the 2,2′-bipyridyl (2b). The unsymmetrical bipyridyl (2b), isolated by preparative t.l.c. exhibited finely split singlets at δ 7.92 and δ 8.62 for the protons in the 3- and 5-positions of the 4,6-diphenylpyridine ring.

Attempts to prepare less symmetrical pyrylium salts (which should be easier to purify), *e.g.* from benzylideneacetone and 2-acetylpyridine or 2-benzylidene-α-tetralone and 2-acetylpyridinium perchlorate, failed. See ref. 6 for further details.



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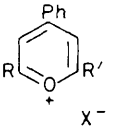
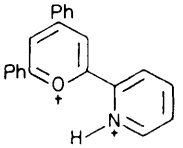


(4)

a; R = R′ = 2-py, X = BF_4
b; R = Ph, R′ = 2-py, X = BF_4
c; R = Ph, R′ = 3-py, X = ClO_4
d; R = Bu^t, R = 3-py, X = ClO_4



(5)

a; X = BF_4
b; CF_3SO_3

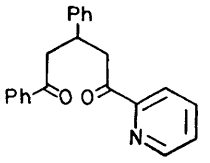
Since the ' one-pot ' method for (4b) from chalcone and acetylpyridine led to mixtures, we allowed 2-acetylpyridine and chalcone to react in ethanolic sodium hydroxide at 20 °C to give 3,5-diphenyl-1-(2-pyridyl)pentane-1,5-dione (6). This was subsequently successfully oxidised by heating it under reflux with chalcone and BF_3·OEt_2 in trifluoroacetic acid to give the pyrylium (5a) as a bistetrafluoroborate salt. This method had previously been applied successfully to the preparation of 2,6-diphenyl-4-(4-pyridinio)pyrylium bistetrafluoroborate.[7] Attempts to cyclise the 1,5-dione using trityl perchlorate–acetic acid [8] failed. Chalcone is known to oxidise 1,5-diones in the ' one-pot ' method.[9]

The dione (6) was also cyclised using trifluoromethanesulphonic acid/2-benzylidene-α-tetralone to give cleanly (although in lower yield) the pyrylium bistrifluoromethanesulphonate (5b).

Reactions of 2-(2-Pyridyl)-4,6-diphenylpyrylium Bistetrafluoroborate.—Pyrylium bistetrafluoroborate (5a)

reacts readily with ammonia to give the bipyridyl (2b), required for kinetic studies.[7]

The pyrylium salt (5a) could be converted into the corresponding pyridinium tetrafluoroborates (7a—h) (see



(6)

Tables 1, 2 and Experimental section). Octylamine however required azeotropic removal of water, in a reaction using ethanol–benzene conditions (yield 63%).

Attempted Intramolecular Nucleophilic Displacements of 2-(2-Pyridyl)pyridinium Salts.—When 1-(4-methoxybenzyl)-2,4-diphenyl-6-(2-pyridyl)pyridinium tetrafluoroborate (7b) was heated at 158 °C for 0.5 h, the rearranged pyridinium (8) was obtained. It is likely that an S_N1 process (as observed in the reaction of 1-(4-methoxybenzyl)-2,4,6-triphenylpyridinium salt with piperidine [10]) produces a carbocation, which is stabilized by the mesomeric effect of the methoxy-group, and which is trapped by the 2-pyridyl nitrogen. A concerted intramolecular S_N2 displacement is unlikely considering Baldwin's rules [11] based on an ideal geometrical approach of the nucleophile and the departure of the leaving group. Evidence for the rearranged pyridinium (8) is provided by its ^{1}H n.m.r. spectrum. The broad signal at δ 8.84 (Table 2) due to the proton α to N in the pyridyl group of (8) is shifted considerably downfield to δ 9.55. This downfield shift caused by quaternisation is considerably more than for protonation, for the H_α and H_β protons on a pyridine ring.[12] The signal at δ 5.84 attributable to the protons of the benzyl C atom is also shifted downfield to δ 6.80.

Kinetic studies [13] on 1-isopropyl-2,4,6-triphenylpyri-

TABLE 1

1-Substituted 2,4-diphenyl-6-(2-pyridyl)pyridinium salts [a]

Compound	Anion	*N*-substituent	Reaction method	Yield (%)	M.p. (°C)	Crystal form	Found (%) C	H	N		Required (%) C	H	N
(7a)	BF_4	$PhCH_2$	A	40	195—199	Prisms	71.3	4.6	5.5	$C_{29}H_{23}BF_4N_2$	71.6	4.7	5.8
(7b)	BF_4	4-OMe·$C_6H_4CH_2$	A	40 [b]	114—115	Micro-prisms	69.6	4.9	5.1	$C_{30}H_{25}BF_4N_2O$	69.8	4.8	5.4
(7c)	CF_3SO_3	$CH_3[CH_2]_6CH_2$	B	63 [c]	137—138	Needles	65.1	5.8	4.8	$C_{31}H_{33}F_3N_2O_3S$	65.3	5.8	4.9
(7d)	BF_4	Bu^n	A	17	203—204	Prisms	69.4	5.7	—	$C_{26}H_{25}BF_4N_2$	69.0	5.5	—
(7e)	BF_4	Pr^i	A	28	222—225	Prisms	68.4	5.3	6.0	$C_{25}H_{23}BF_4N_2$	68.5	5.3	6.4
(7f)	CF_3SO_3	$PhCH_2CH_2$	A	62 [d]	169.5—171.5	Prisms	65.9	4.6	4.9	$C_{31}H_{25}F_3N_2O_3S$	66.2	4.5	5.0
(7g)	CF_3SO_3	4-ClC_6H_4·CH_2CH_2	B	62	145—147	Prisms	62.0	4.0	4.6	$C_{31}H_{24}ClFN_2O_3S$	62.4	4.0	4.7
(7h)	BF_4	Ph	A	86	228—231	Prisms	69.6	4.3	—	$C_{28}H_{21}BF_4N_2$, $0.5H_2O$	69.8	4.4	—
(7i)	CF_3SO_3	$CH(OMe)_2CH_2$	A	53 [c]	154—155	Micro-crystals	59.0	4.5	4.8	$C_{27}H_{25}F_3N_2SO_5$	59.4	4.6	5.1

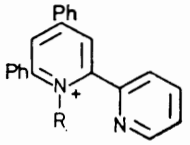
[a] Recrystallised from absolute EtOH unless otherwise indicated. [b] Recrystallised from absolute EtOH–CCl_4 (3 : 10). [c] Crude product pure. [d] Recrystallised from 95% EtOH.

TABLE 2

^{1}H N.m.r. spectra (δ) of *N*-substituted 2,4-diphenyl-6-(2-pyridyl)pyridinium salts

Compound	Anion (X)	Solvent	R	Aryl protons	1-Subst.	6-H of 2-pyridyl groups
(7a)	BF_4	$CDCl_3$	$PhCH_2$	7.60—8.09 (15 H, m)	5.90 (2 H, s), 6.73 (3 H, m), 7.20 (2 H, m)	8.75 (1 H, m)
(7b)	BF_4	$(CD_3)_2SO$	4-$MeOC_6H_4CH_2$	7.73—8.32 (15 H, m)	3.67 (3 H, s), 5.84 (2 H, s), 6.65 (4 H, m)	8.65 (1 H, m)
(7c)	CF_3SO_3	$CDCl_3$	$CH_3(CH_2)_7$	7.65—8.40 (15 H, m)	0.90—1.64 (15 H, m), 4.49 (2 H, t)	8.78 (1 H, m)
(7d)	BF_4	$(CD_3)_2CO$–CF_3CO_2H	Bu^n	7.73—8.52 (15 H, m)	0.60—1.70 (7 H, m) 4.70 (2 H, t)	8.64 (1 H, m)
(7e)	BF_4	$CDCl_3$–CF_3CO_2H	Pr^i	7.60—8.25 (15 H, m)	1.50 (6 H, d, *J* 3.5 Hz) 5.05 (1 H, h, *J* 3.5 Hz)	8.74 (1 H, m)
(7f)	CF_3SO_3	$(CD_3)_2SO$	$PhCH_2CH_2$	7.80—8.63 (15 H, m)	2.83 (2 H, t) 4.70 (2 H, t), 6.55 (2 H, m), 7.20 (3 H, m)	8.99 (1 H, m)
(7g)	CF_3SO_3	$CDCl_3$	4-$ClC_6H_4CH_2CH_2$	7.68—8.40 (15 H, m)	2.90 (2 H, t), 4.65 (2 H, t), 6.30—7.06 (4 H, ABq)	8.70 (1 H, m)
(7h)	BF_4	CF_3CO_2H	Ph	7.28—8.60 (20 H, m)		8.95 (1 H, m)
(7i)	CF_3SO_3	$CDCl_3$	$CH(OMe)_2CH_2$	7.68—8.21 (15 H, m)	2.95 (6 H, s), 4.20 (1 H, t, *J* 2.7 Hz), 8.80 (1 H, d), 4.96 (2 H, d, *J* 2.7 Hz)	8.80 (1 H, d)

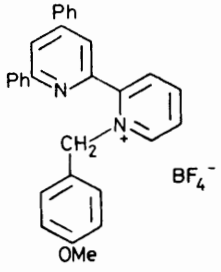
dinium tetrafluoroborate have shown this compound to have considerable S_N1 character in its reaction with piperidine. Thus the corresponding 2-(2-pyridyl)isopropylpyridinium tetrafluoroborate (7e) was heated in



(7) X^-

R	X	R	X
a; $PhCH_2$	BF_4	f; $PhCH_2CH_2$	CF_3SO_3
b; 4-MeO-$C_6H_4CH_2$	BF_4	g; 4-$ClC_6H_4CH_2$	CF_3SO_3
c; $CH_3(CH_2)_7$	CF_3SO_3	h; Ph	BF_4
d; Bu^n	BF_4	i; $CH(OMe)_2CH_2$	$CF_3SO_3^-$
e; Pr^i	BF_4		

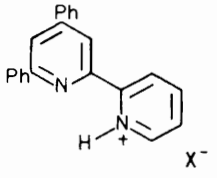
dimethyl sulphoxide at 100 °C for 9.5 h to effect the movement of the substituent to the 2-pyridyl nitrogen [*cf.* as that observed for the 4-methoxybenzyl case (7b)]. The product however was bipyridyl (9a) as the tetrafluoroborate salt. Evidently an elimination process is



(8)

occurring, although the 1-benzylpyridinium (7a) likewise gave the bipyridyl (9a) when heated.

Elimination (Hofmann-type) Reactions.—1-(2-Phenylethyl)- and 1-(2-*p*-chlorophenylethyl)-2,4-diphenyl-6-(2-pyridyl)pyridiniums, (7f) and (7g) gave on pyrolysis at



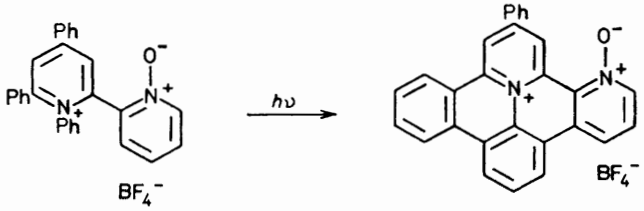
(9)

a; X = BF_4

b; X = CF_3SO_3

259 °C/0.3 mmHg and 260 °C/1 mmHg styrene (71%) and 4′-chlorostyrene (70%) respectively as distillates. The protonated bipyridyl (9b) was isolated from the pot residue. The 1-octyl derivative (7c) gave on pyrolysis at 165 °C/0.15 mmHg a mixture of oct-1- and *cis*- and *trans*-oct-2-enes in yields of 40 and 22% respectively, as deduced by ^{13}C n.m.r. spectroscopy and g.l.c. Clearly, an *E*1 process is operating,[14] rather than the expected *E*2 required for clean formation of oct-1-ene.

Other Reactions of 4,6-Diphenyl-2-(2-pyridyl)pyridinium Salts.—The α-methylene protons of benzylpyridiniums are removed by base to give zwitterions, which react with electrophiles (E^+) to yield adducts.[15] However, similar reactions were initially unsuccessful with a 1-benzyl-2,4,6-triphenylpyridinium cation [16] in which it was considered that the flanking phenyls hindered the approach of electrophile.

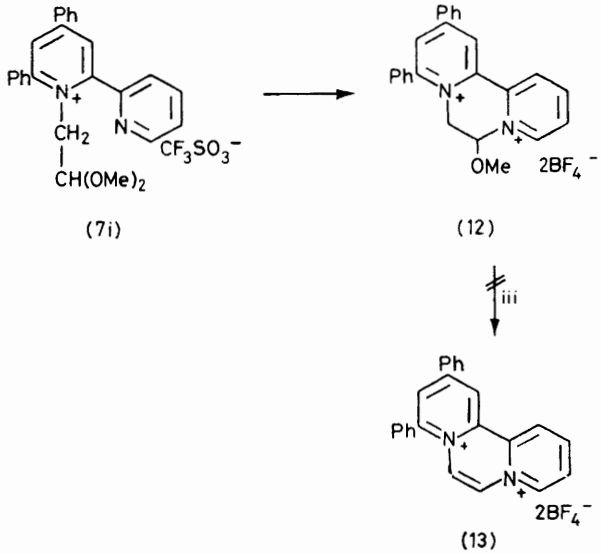


(10) (11)

With a 2-(2-pyridyl) group, co-ordination of E^+ with the pyridyl nitrogen could ease attack. Refluxing acetic anhydride–potassium acetate decomposed the benzyl compound (7a) into the bipyridyl (2b) and benzyl acetate, as observed previously under pyrolysis conditions.[17] Compound (7d) did not react.

Grignard reagents add nucleophilically to 1-alkyl-2,4,6-triphenylpyridiniums at the 2- and 4-positions to give 1,2- and 1,4-adducts.[18] A 2-(2-pyridyl) group could co-ordinate the Grignard reagent and position it for nucleophilic displacement of the *N*-substituent. However, ethylmagnesium bromide and α-phenylethylmagnesium bromide in THF gave with the 1-benzyl salt (7a) respectively 68 and 62% of the bipyridyl (2a). Small amounts (*ca.* 28%) of the 2- and 4-adducts were identified by ^1H n.m.r. in the crude mixture.

1-Phenyl-2,4-diphenyl-6-(2-pyridyl)pyridinium (7h)

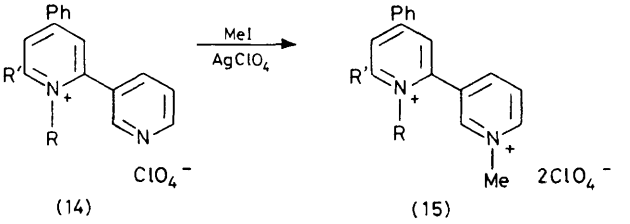


(7i) (12) (13)

Reagents: i, HCl–MeOH; ii, HBF_4; iii, HCl and heat or H_2SO_4 and heat

was oxidised with trifluoroperacetic acid to the *N*-oxide (10). Photolysis of 2-(1-oxido-2-pyridyl)-1,4,6-triphenylpyridinium tetrafluoroborate (10) gave the bis-cyclised product (11) instead of inducing attack of the *N*-oxide at the *N*-phenyl group. In an attempt to prepare the dipyridopyrazine (13), the 1,2-dimethoxyethylpyridinium (7i) was refluxed in concentrated HCl to give compound (12). Further acidification failed to give (13).

2-(3-*Pyridyl*)*pyrylium Salts*.—3-Acetylpyridinium perchlorate reacted with chalcone [19] and t-butyl styryl ketone [20] to yield the 2-(3-pyridyl)pyrylium salts (4c) (36%) and (4d) (57%) respectively, which were characterized by elemental analyses and spectral data. Anhydrous ammonia with pyrylium salt (4b) afforded the pyridine (2d).



a; R' = Ph, R = $PhCH_2$
b; R' = Bu^t, R = Bu^n

Benzylamine and salt (4c) gave the 1-benzylpyridinium salt (14a), which with methyl iodide and the silver perchlorate–acetonitrile complex gave the *N*-methyl bis-quaternary salt (15a) (90%). The bis salt (15a) was characterised on the basis of spectral data: notably singlets at δ 4.5 and 5.7, for the *N*-methyl and *N*-benzyl protons. Similarly n-butylamine and salt (4d) gave the 1-n-butylpyridinium salt (14b) converted by methyl iodide and silver perchlorate–acetonitrile into the bis-perchlorate (15b) (79%).

EXPERIMENTAL

Melting points are uncorrected and were measured on a Reichert microscope hot stage. I.r. and 60 MHz ^1H n.m.r. spectra were recorded on a Perkin-Elmer 257 grating i.r. spectrometer, R 12 Perkin-Elmer n.m.r. spectrometer, and HA-100 Varian n.m.r. spectrometer respectively. N.m.r. measurements used $SiMe_4$ as internal standard. Mass spectra were done on a RMU-6E Hitachi Perkin-Elmer spectrometer. G.l.c. analyses were performed with a Perkin-Elmer F11 gas chromatograph (flame ionisation; stationary phase OV 1, oven temperatures of 50 °C).

The following were made by the literature methods indicated: 2-acetylpyridine [21] (65%), b.p. 188—189 °C at 760 mmHg (lit.,[22] b.p. 192—193 °C at 760 mmHg); 2-pyridyl styryl ketone (20%), m.p. 59—60 °C (lit.,[5] m.p. 71 °C); and 2-benzylidene-α-tetralone [23] (85%), m.p. 104—105 °C (lit.,[23] m.p. 105 °C).

2,4-*Diphenyl*-6-(2-*pyridyl*)*pyrylium Tetrafluoroborate* (4b) *and* 2,4-*Diphenyl*-6-(2-*pyridyl*)*pyridine* (2b).—(i) Chalcone (2.1 g, 10 mmol) and 2-acetylpyridine (1.2 g, 10 mmol) were heated at 100 °C for 30 min in BF_3·OEt_2 (14 g, 40 mmol). The mixture was treated with 10% aqueous HBF_4 (40 ml) and extracted with C_6H_6 (20 ml). The aqueous layer was evaporated at 100 °C/120 mmHg. Addition of Et_2O (30 ml) and crystallisation from EtOH gave *pyrylium salt* (4b) as yellow prisms (0.99 g, 25%) m.p. 273—276 °C; $\nu_{max.}$ ($CHBr_3$) 1 630s, 1 590m, and 1 580m cm^{-1}; δ [$(CD_3)_2SO$, 100 MHz] 7.82 (7 H, m), 8.28 (1 H, t, *J* 6 Hz), 8.60 (5 H, m), and 9.02—9.28 (3 H, m). Conversion of salt (4b) into the corresponding pyridine (2b) was effected by action of anhydrous ammonia as described below. T.l.c. [Kieselgel F254; light petroleum (b.p. 40—60 °C)–EtOAc (3 : 1)] showed 2,4,6-triphenylpyridine (2a) as a minor component.

(ii) 2-Pyridyl styryl ketone (0.6 g, 2.9 mmol), acetophenone (0.35 g, 2.9 mmol), and BF_3·OEt_2 (4.5 g, 14.5 mmol) were heated at 100 °C for 1 h with stirring. After cooling, Me_2CO (5 ml) and then Et_2O (5 ml) were added. The resulting crystals were suspended in EtOH and anhydrous ammonia bubbled through for 30 min.

The product was purified by thick-layer chromatography [Kieselgel PF254; light petroleum (b.p. 40—60 °C)–EtOAc (20 : 1)] to give *pyridine* (2b) as needles [from light petroleum (b.p. 80—100 °C)], m.p. 157.5—158 °C (Found: C, 85.6; H, 5.3; N, 9.1. $C_{22}H_{16}N_2$ requires C, 85.7; H, 5.2; N, 9.1%); $\nu_{max.}$ ($CHBr_3$) 1 605m, 1 590s, 1 575m, and 1 560m cm^{-1}; *m/e* (70 eV) 77(3), 102(3), 153(4), 154(5), 202(5), 203(4), 204(5), 230(30), 231(18), 280(10), 307(42), 308(100), and 309(36%).

3,5-*Diphenyl*-1-(2-*pyridyl*)*pentane*-1,5-*dione* (6).—2-Acetylpyridine (4.08 g, 33.65 mmol), sodium hydroxide (4 g), (7.00 g, 33.65 mmol), EtOH (7 ml) and H_2O (8 ml) were refluxed for 20 min and then poured into water (15 ml). A gum that settled out was dissolved in hot EtOH (10 ml), and the solution filtered and stirred at 20 °C. The white microcrystals of the 1,5-*diketone* precipitated out (4.81 g, 43%), m.p. 92—100 °C (EtOH) (Found: C, 80.3; H, 5.8; N, 4.4. $C_{22}H_{19}NO_2$ requires C, 80.2; H, 5.8; N, 4.3%); $\nu_{max.}$ ($CHBr_3$) 1 685vs, 1 595s, 1 585s, and 1 570sh cm^{-1}; δ ($CDCl_3$, 60 MHz) 3.60 (4 H, d), 4.20 (1 H, m), 7.00—8.05 (13 H, m), and 8.65 (1 H, br); *m/e* (70 eV) 329 (mol ion peak), 223, and 224.

4,6-*Diphenyl*-2-(2-*pyridinio*)*pyrylium Bistetrafluoroborate* (5a).—3,5-Diphenyl-1-(2-pyridyl)pentane-1,5-dione (6) (17.42 g, 52.95 mmol) and 2-benzylidene-α-tetralone (12.39 g, 52.95 mmol) were refluxed with BF_3·OEt_2 (28.3 ml, 211.80 mmol) in CF_3CO_2H (7 ml) at 100 °C for 6 h. The resulting dark green gummy mixture was dissolved in hot glacial AcOH (10 ml), and the required *pyrylium salt* was precipitated by stirring in Et_2O. The crude product (25.31 g, 99%) was recrystallised from HBF_4–EtOH (1 : 1) to afford yellow prisms, m.p. 256 °C (decomp.) (Found: C, 54.1; H, 3.5. $C_{22}H_{17}B_2F_8NO$ requires C, 54.4; H, 3.5%); $\nu_{max.}$ (Nujol) 1 630vs, 1 609sh, 1 595s, and 1 580vs cm^{-1}; δ [$(CD_3)_2SO$, 60 MHz] 6.70—9.31 (17 H, m).

4,6-*Diphenyl*-2-(2-*pyridinio*)*pyrylium Bistrifluoromethanesulphonate* (5b).—3,5-Diphenyl-1-(2-pyridyl)pentane-1,5-dione (6) (5.0 g, 15.20 mmol) and 2-benzylidene-α-tetralone (3.56 g, 15.20 mmol) were dissolved in AcOH (10 ml). Trifluoromethanesulphonic acid (2.7 ml, 30.6 mmol) was added and the solution refluxed for 7 h at 100 °C. The solution was cooled, Et_2O (20 ml) added, and the mixture stirred. The yellow *pyrylium salt* (5b) which precipitated out of solution was filtered off and washed twice with Et_2O (2 × 7 ml). The crude product (4.95 g, 53%) was recrystallised from glacial AcOH to afford orange needles, m.p. 286—289 °C (Found: C, 46.8; H, 2.7. $C_{24}H_{17}F_6NO_7S_2$ requires C, 47.3; H, 2.8%); $\nu_{max.}$ ($CHBr_3$) 1 630vs, 1 625sh, 1 595vs, 1 580s, 1 550w, 1 510s, 1 470w, 1 415w,

1 260br, s, and 1 030vs cm^{-1}; δ [$(CD_3)_2SO$, 60 MHz] 6.71—9.21 (17 H, m).

2,4-*Diphenyl*-6-(2-*pyridyl*)*pyridine* (2b).—4,6-Diphenyl-2-(2-pyridinio)pyrylium bistetrafluoroborate (5a) (0.63 g, 1.3 mmol) was suspended in ' super dry ' EtOH (5 ml). Anhydrous ammonia (0.36 ml, 6.49 mmol) was added. The mixture, a deep red colour, was stirred for 1 h after which time H_2O (2 ml) was added. The mixture was then stirred overnight. The white crystalline solid that precipitated out was filtered off (0.38 g, 95%) and recrystallised from 95% EtOH to afford white *prisms*, m.p. 149 °C (Found: C, 85.4; H, 5.0; N, 8.9. $C_{22}H_{16}N_2$ requires C, 85.7; H, 5.2; N, 9.1%); $\nu_{max.}$ ($CHBr_3$) 1 606sh, 1 590w—m, 1 585vs, 1 566s, 1 547s, 1 495m, 1 470m, 1 450w, 1 440sh, 1 395vs, 1 295s, 880s, 790vs, 760vs, and 735 cm^{-1}; $\lambda_{max.}$ (PhCl) 313 nm (ε 12 500); δ [$CDCl_3$, 100 MHz] 7.20—8.20 (15 H, m) and 8.65 (1 H, d).

General Methods of Preparation of Pyridinium Salts (7a—h).—*Method A*. To the appropriate pyrylium tetrafluoroborate or trifluoromethanesulphonate (3.8 mmol) suspended in CH_2Cl_2 (10 ml) was added amine (7.6 mmol). After *ca.* 0.5 h Et_2O (*ca.* 15 ml) was added and the solution stirred at 20 °C overnight. The white crystalline solid was then filtered off.

Method B. The appropriate pyrylium trifluroromethanesulphonate (3.8 mmol) was refluxed in a 1 : 1 mixture (8 ml) of ' super dry ' EtOH–dry benzene for *ca.* 11 h. The solvent was stripped off at 20 mmHg/40 °C. Alternatively the solvent was slowly distilled off (azeotropic removal of water). The residue was triturated with Et_2O (*ca.* 10 ml). The pure crystalline solid that precipitated out of solution was filtered off.

Pyrolysis of 1-(4-*Methoxybenzyl*)-2,4-*diphenyl*-6-(2-*pyridyl*)*pyridinium Tetrafluoroborate* (7b).—A dried (P_2O_5, 50 °C/5 mmHg) sample of pyridinium tetrafluoroborate (7b) (0.13 g, 0.25 mmol) was heated to 158 °C for 0.5 h in a 15 mm diameter cylindrical tube. The resulting black mass was recrystallised from absolute EtOH to give 2-(4,6-diphenyl-2-pyridyl)-1-(4-methoxybenzyl)pyridinium tetrafluoroborate (8) (0.13 g, 0.25 mol, 100%) as white microcrystals, m.p. 92—99 °C (Found: C, 69.4; H, 4.7; N, 5.2. $C_{30}H_{25}BF_4N_2O$ requires C, 69.8; H, 4.8; N, 5.4%); ν ($CHBr_3$) 3 170—3 100 (w, mult.), 2 950—2 900 (m, mult.), 2830s, 1 630sh, 1 610s, 1 600vs, 1 585m, 1 550s, 1 530s, 1 500vs, 1 465s, 1 440s, 1 420s, 1 405s, 1 370m, 1 300m, 1 245b, 1 060s, br, 920w, 875m, 810m, 785m, and 755vs; δ [$(CD_3)_2SO$, 100 MHz] 3.65 (3 H, s), 6.80 (2 H, q), 7.50—9.05 (19 H, m), and 9.55 (1 H, b).

2-(1-*Oxido*-2-*pyridyl*)-1,4,6-*triphenylpyridinium Tetrafluoroborate* (10).—The pyridinium salt (7h) (2.0 g, 4.24 mmol), CF_3CO_2H (13.4 ml), and H_2O_2 (30%) (1.34 g) were refluxed on a steam-bath for 3 h. The solution was then diluted with H_2O (200 ml). The filtrate was evaporated to small bulk at 35 °C at 20 mmHg. Water (200 ml) was added to the residue and the evaporation process continued. The procedure was repeated a third time. To the final residue, $CHCl_3$ (30 ml) was added in the presence of anhydrous $NaHCO_3$. The mixture was filtered, and the filtrate evaporated to dryness under reduced pressure (2.5 g, 72%). Recrystallisation from isopropyl alcohol afforded white *microprisms* of (10), m.p. 275 °C (Found: C, 69.3; H, 4.4; N, 6.1. $C_{28}H_{21}BF_4N_2O$ requires C, 68.9; H, 4.3; N, 5.7%), $\nu_{max.}$ ($CHBr_3$) 1 620vs, 1 585s, and 1 550s cm^{-1}; δ ($CDCl_3$, 100 MHz) 7.00—8.20 (20 H, m) and 8.45 (1 H, d).

Photolytic Reaction of 2-(1-*Oxido*-2-*pyridyl*)-1,4,6-*triphenylpyridinium Tetrafluoroborate* (10).—2-(1-Oxido-2-pyridyl)-1,4,6-triphenylpyridinium tetrafluoroborate (10) (2.0 g, 4.10 mmol) was dissolved in absolute MeOH (200 ml) and photolysed in a quartz vessel for 2 h. Evaporation of the solvent gave a dark gum. Recrystallisation from absolute EtOH gave the N-*oxide* (11) (1.7 g, 86%) as yellow needles, m.p. 245—255 °C (Found: C, 69.6; H, 3.2; N, 5.4. $C_{28}H_{17}BF_4N_2O$ requires C, 69.4; H, 3.5; N, 5.8%); $\nu_{max.}$ ($CHBr_3$) 1 630vs, 1 624sh, and 1 605 cm^{-1}.

9,10-*Dihydro*-9-*methoxy*-1,3-*diphenyl*-8a,10a-*diazoniophenanthrene Bistetrafluoroborate* (12).—1-(2,2-Dimethoxyethyl)-2,4-diphenyl-6-(2-pyridyl)pyridinium trifluoromethanesulphonate (7i) (0.82 g, 1.50 mmol) was refluxed with concentrated HCl (0.11 g, 3.0 mmol) in MeOH (2 ml) for 4.25 h. The solvent was stripped off at 20 mmHg/*ca.* 40 °C. Excess of HBF_4 (*ca.* 0.5 ml) was added and the yellow oil triturated with Et_2O. The white product that precipitated out was the required product (12) (0.74 g, 91%); it was recrystallised from EtOH to afford white needles, m.p. 228—232.5 °C (Found: C, 55.5; H, 4.0; N, 5.1. $C_{25}H_{22}B_2F_8N_2O$ requires C, 55.6; H, 4.1; N, 5.2%); $\nu_{max.}$ ($CHBr_3$) 1 630vs, 1 620s, 1 600w, 1 585vs, 1 562s, 1 510vs, 1 464w, 1 445m, s, 1 418m, s, 1 375m, s, 1 350s, 1 270s, 1 245m, 1 050br, vs, 880s, 820m, s, 770vs, and 755 vs cm^{-1}; δ [$(CD_3)_2SO$, 100 MHz] 3.42 (3 H, s), 5.22 (1 H, br), 6.49 (2 H, br), 7.70 (12 H, m), 8.37—9.40 (3 H, m), and 9.70 (1 H, d).

3-*Acetylpyridinium Perchlorate*.—70% Perchloric acid (30 g, 0.42 mol) was added dropwise at 0 °C to 3-acetylpyridine (24.2 g, 0.2 mol) in EtOH (50 ml). Et_2O (150 ml) was then added; after 2 h at 0 °C filtration and washing with Et_2O (200 ml), gave the *perchlorate* (39.3 g, 89%) which crystallised from EtOH as needles, m.p. 106—108 °C (Found: C, 37.8; H, 3.6; N, 6.7. $C_7H_8ClNO_5$ requires C, 37.9; H, 3.6; N, 6.3%); $\nu_{max.}$ ($CHBr_3$) 3 220s, 3 185m, 3 120m, 3 080m, 1 695s, 1 630m, and 1 600s cm^{-1}; δ (CF_3CO_2H, 60 MHz) 3.0 (3 H, s) and 8.5—9.5 (5 H, m).

2-*Acetylpyridinium perchlorate* (prepared similarly) formed needles (89%) (from EtOH), m.p. 187—188 °C (Found: C, 37.9; H, 3.7; N, 6.5. $C_7H_8ClNO_5$ requires C, 37.9; H, 3.6; N, 6.3%); $\nu_{max.}$ ($CHBr_3$) 1 715s and 1 630m cm^{-1}; δ (CF_3CO_2H, 60 MHz) 3.0 (3 H, s) and 8.5—9.5 (4 H, m).

2-*t*-*Butyl*-4-*phenyl*-6-(3-*pyridyl*)*pyrylium Perchlorate* (4d).—72% Perchloric acid (6.3 g, 45 mmol) was added dropwise to 3-acetylpyridinium perchlorate (10 g, 45 mmol) and t-butyl styryl ketone (17 g, 90 mmol) at 100 °C. After 1 h at 100 °C and cooling, Et_2O (100 ml) was added. The solid was filtered off, washed with EtOAc (20 ml) and crystallised from MeOH to give *salt* (4d) as yellow needles (10.3 g, 57%), m.p. 234—235 °C (decomp.) (Found: C, 61.1; H, 5.1; N, 3.7. $C_{20}H_{20}ClNO_5$ requires C, 61.6; H, 5.2; N, 3.6%); $\nu_{max.}$ ($CHBr_3$) 3 080w, 2 980w, 2 930w, 1 630s, 1 600s, and 1 580w cm^{-1}; δ [$(CD_3)_2SO$, 100 MHz] 1.54 (9 H, s), 7.78 (5 H, m), 8.49 (1 H, m), 8.57 (1 H, d, *J* 1.5 Hz), 8.82 (1 H, dt, J_1 8 Hz, $J_2 = J_3 = 2$ Hz), 8.98 (1 H, dd, J_1 5 Hz, J_2 2 Hz), 9.22 (1 H, d, *J* 1.5 Hz), and 9.67 (1 H, d, *J* 2 Hz).

2-*t*-*Butyl*-4-*phenyl*-6-(3-*pyridyl*)*pyridine* (2d).—Treatment of (4d) with ammonia by the usual procedure gave the *pyridine* (2d) (67%) as needles from light petroleum (b.p. 80—100 °C), m.p. 107—108 °C (Found: C, 83.3; H, 7.0; N, 9.7. $C_{20}H_{20}N_2$ requires C, 83.0; H, 6.8; N, 9.7%); $\nu_{max.}$ ($CHBr_3$) 3 120m, 2 960s, 2 930m, 2 830w, 1 605s, and 1 560s cm^{-1}; δ ($CDCl_3$, 100 MHz) 1.47 (9 H, s), 7.2—7.6 (7 H, m), 7.71 (1 H, d, *J* 2 Hz), 8.42 (1 H, dt, J_1 8 Hz; $J_2 = J_3 = 2$ Hz), 8.61 (1 H, dd, J_1 5 Hz, J_2 2 Hz), and 9.33 (1 H, d, *J* 2

Hz); *m/e* (70 eV) 274(100), 275(68), 276(10), 287(82), 288(95), 289(60), and 290(6%).

2,4-*Diphenyl*-6-(3-*pyridyl*)*pyrylium Perchlorate* (4c).—70% Perchloric acid (3.2 g, 22 mmol) was added dropwise to 3-acetylpyridinium perchlorate (5 g, 22 mmol) and chalcone (7 g, 30 mmol) at 80 °C. The stirred mixture was kept at 100 °C for 10 min after which cooled Me_2CO (40 ml) was added to give 3-acetylpyridinium perchlorate (25) (first crop 3.2 g). Addition of more Et_2O gave a second crop (2.15 g) which crystallised from EtOH as yellow prisms (4.9 g, 36%), m.p. 277—279 °C (decomp.) (Found: N, 10.3. $C_{22}H_{16}ClNO_5$ requires N, 10.4%); $\nu_{max.}$ ($CHBr_3$) 1 620s, 1 590s, and 1 575w cm^{-1}; δ (CF_3CO_2H, 60 MHz) 8.9 (6 H, m), 8.4 (4 H, m), 8.9 (2 H, m), 9.2 (2 H, m), 9.5 (1 H, m), and 9.7 (1 H, s).

1-*Benzyl*-2,4-*diphenyl*-6-(3-*pyridyl*)*pyridinium Perchlorate* (14a).—Benzylamine (1.26 g, 12 mmol) was stirred at 25 °C with pyrylium salt (4c) (2 g, 4 mmol) in EtOH (8 ml) for 12 h. The *salt* (14a) was filtered off, washed with Et_2O (2 × 20 ml) and crystallised from EtOH as prisms (1.5 g, 75%), m.p. 187—188 °C (Found: C, 69.9; H, 4.6; N, 5.6. $C_{29}H_{23}ClN_2O_4$ requires C, 69.8; H, 4.6; N, 5.6%); $\nu_{max.}$ ($CHBr_3$) 1 620s, 1 580s, and 1 560m cm^{-1}; δ [$(CD_3)_2SO$, 100 MHz] 5.69 (2 H, s), 6.68 (2 H, m), 7.18 (2 H, m), 7.63 (11 H, m), 8.11—8.30 (3 H, m), 8.62 (2 H, s), and 8.78 (1 H, m).

1-*Benzyl*-2-(1-*methyl*-3-*pyridinio*)-4,6-*diphenylpyridinium Bisperchlorate* (15a).—MeI (4.3 g, 30 mmol) was added to $AgClO_4$ (0.2 g, 10 mmol) and pyridinium perchlorate (14a) (3 g, 6 mmol) in MeCN (20 ml) and the mixture was stirred at 20 °C for 12 h. AgI was filtered off and washed with MeCN (2 × 10 ml). The filtrate was evaporated at 20 mmHg. The *salt* (15a) crystallised from EtOH as prisms (3.3 g, 90%), m.p. 185—185.5 °C (Found: N, 4.3. $C_{30}H_{26}Cl_2N_2O_8$ requires N, 4.6%); $\nu_{max.}$ ($CHBr_3$) 1 650m, 1 630s, 1 600m, and 1 570m cm^{-1}; δ (CF_3CO_2H, 60 MHz) 4.5 (3 H, s), 5.7 (2 H, s), and 7.0—9.0 (21 H, m).

1-*n*-*Butyl*-2-*t*-*butyl*-4-*phenyl*-6-(3-*pyridyl*)*pyridinium Perchlorate* (14b).—This compound was prepared similarly to salt (14a) using n-butylamine and was obtained as plates (62%) (from EtOAc), m.p. 155—158 °C (Found: C, 64.4; H, 6.6; N, 6.7. $C_{24}H_{29}ClN_2O_4$ requires C, 64.8; H, 6.6; N, 6.3%); $\nu_{max.}$ ($CHBr_3$) 2 690m, 2 930m, 1 630s, 1 592m, and 1 570s cm^{-1}; δ ($CDCl_3$, 100 MHz) 0.63 (3 H, t, *J* 7 Hz), 1.06 (2 H, q, *J* 7 Hz), 1.7 (2 H, m), 1.72 (9 H, s), 4.68 (2 H, t, *J* 8 Hz), 7.5—7.7 (7 H, m), 8.12 (1 H, d, *J* 6 Hz), and 8.81 (1 H, s).

1-*n*-*Butyl*-2-(1-*methyl*-3-*pyridinio*)-4-*phenyl*-6-*t*-*butylpyridinium Bisperchlorate* (15b).—The pyridinium salt (14b) was methylated in a manner similar to that for the bisperchlorate (15a). The *salt* (15b) crystallised as prisms (79%) (from EtOH), m.p. 252—253 °C (decomp.) (Found: C, 53.7; H, 5.8; N, 5.1. $C_{25}H_{32}N_2O_8$ requires C, 53.7; H, 5.8; N, 5.0%); $\nu_{max.}$ ($CHBr_3$) 3 060m, 2 960m, 1 645s, 1 625s, 1 600m, and 1 570s cm^{-1}.

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