Nucleophilic Displacements of *N*-Aryl and Heteroaryl Groups. Part 6. The Rearrangement of 1-Aryl-5,6,7,8-tetrahydro-8-oximino-2,6-diphenylquinolinium Cations[1]

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1-Aryl-2-(benzyl- and neopentyl-carbamoyl) pyridinium salts (**7**) are rearranged by NaH at 110 °C into the corresponding 2-(*N*-aryl-*N*-substituted carbamoyl) pyridines (**19**). The 1-aryl-5,6,7,8-tetrahydro-8-oximinoquinolinium salts (**14**) similarly give 8-(arylhydroxyamino)-5,6-dihydroquinolines (**17**), preferring a five- to a six-membered transition state.

The conversion of primary arylamines into other functionalities has recently been achieved under relatively mild conditions (110—150 °C), with mediation by pyrylium salts.[2–4] In this way, phenols,[2] diarylamines[3] and aryl sulphides[4] were prepared *via* intramolecular rearrangements of (**1**)—(**3**), respectively.

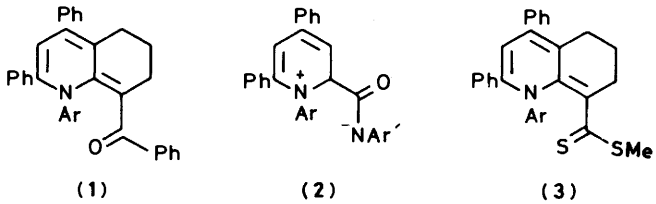
In a continuation of this work, we now report preparative and intramolecular aryl rearrangement studies carried out on *N*-arylpyridinium salts containing a substituted carbamoyl group (**7**) or a hydrazidocarbonyl group (**8**) at the 2-position of the pyridinium ring, and on 8-substituted 1-aryl-5,6,7,8-tetrahydroquinolinium salts [*cf.* (**10**)].

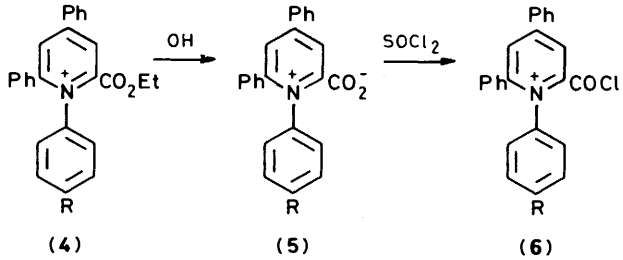
Preparation of 1-*Aryl*-2-(N-*substituted carbamoyl*)- (**7**) *and* 2-(*Substituted hydrazidocarbonyl*)-4,6-*diphenylpyridinium Salts* (**8**).—1-Aryl-2-ethoxycarbonyl-4,6-diphenylpyridinium tetrafluoroborates (**4**) were converted into the corresponding pyridinium acid chlorides (**6**) *via* the pyridinium betaines (**5**).[3] The reaction of (**6a**) and (**6b**) with benzylamine and neopentylamine gave the 2-(*N*-substituted carbamoyl)-pyridinium salts (**7a—d**), and with hydrazines (at 0 °C) (**6a—d**) gave the 2-(substituted hydrazidocarbonyl)pyridinium salts (**8a—g**) (Table 1). A complex mixture was obtained from the reaction of methylhydrazine with (**6b**) in the usual way; however, if the acid chloride (**6b**) was added slowly to a dichloromethane solution of methylhydrazine, the expected product (**8e**) was isolated.

The pyridinium salts (**7**) and (**8**) show characteristic i.r. and n.m.r. spectra: ν(C=O) occurs at 1 685 cm^{-1} in (**7**) and at 1 680 cm^{-1} in (**8**). The ^1H n.m.r. spectra of the carbamoyl derivatives show in the range δ 3—4 the benzylic methylene protons coupled with the NH proton (*J* 6 Hz). The hydrazido-carbonyl derivatives (**8**) show characteristic patterns[3] of 2-substituted 1-aryl-4,6-diphenylpyridinium salts (Table 2).

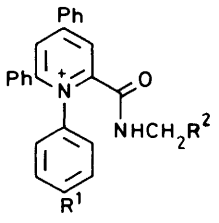
Preparation of 8-*Substituted* 1-*Aryl*-5,6,7,8-*tetrahydroquinolinium Cations*.—The anhydro bases (**13c—f**) were prepared as described previously[5] from the quinolinium cations (**10c—f**). The 8-methylchromenylium compound (**9b**)[6] gave successively the quinolinium salt (**10g**) and anhydro base (**13g**). The anhydrobase (**13c**) reacted with phenacyl bromide and with ethyl bromoacetate to give the new quinolinium salts (**11i**) and (**11h**), respectively, and (**13g**) similarly gave (**11j**) (Scheme).

The chromenylium salt (**9**) readily gave the dimethylaminomethylene derivative (**12r**) by Reynolds and Van Allan's method;[7] however, reaction of this with primary amines occurred with substitution of the NMe_2 group to give (**12r—v**), leaving the heterocyclic oxygen untouched[8] (Table 3), instead of resulting in the expected pyridinium salts. This was shown by elemental analyses and confirmed by the ^1H n.m.r. spectra (Table 4).

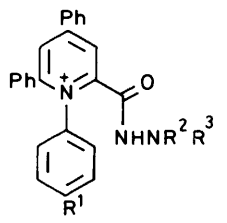




In (**4**)—(**6**) a, R = H; b, R = Me; c, R = Cl; d, R = Ph



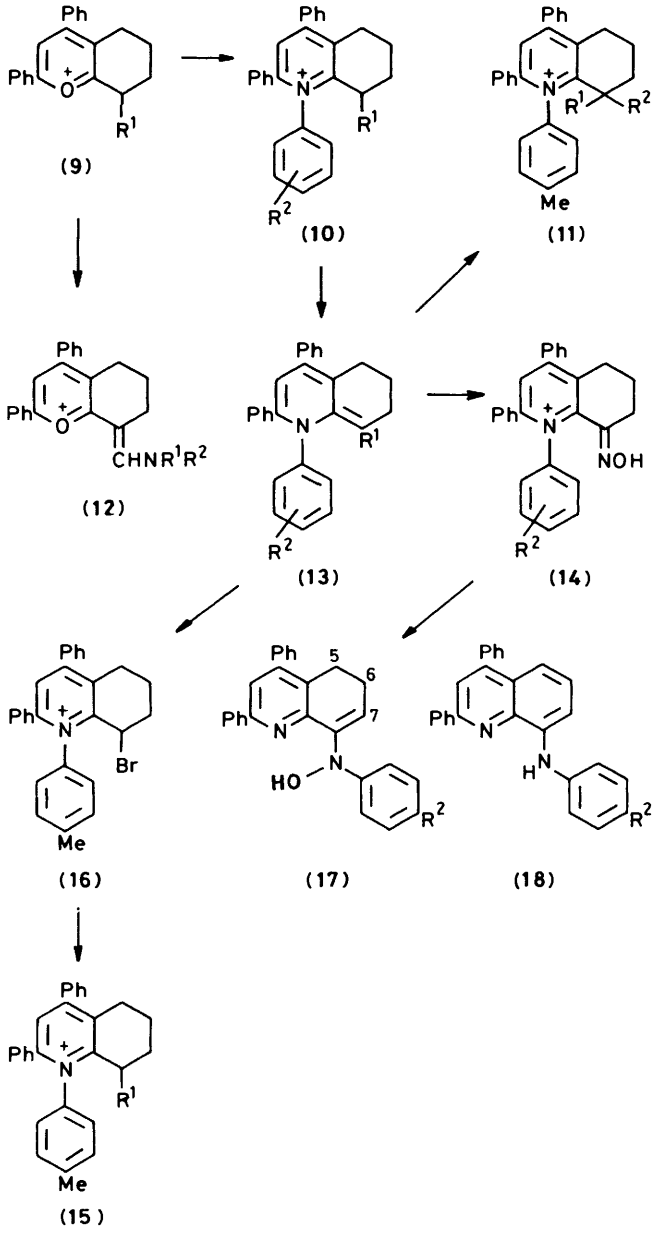
	R^1	R^2
a;	H	Ph
b;	Me	Ph
c;	H	Bu^t
d;	Me	Bu^t



	R^1	R^2	R^3
a;	H	H	Ph
b;	Me	H	Ph
c;	Cl	H	Ph
d;	Ph	H	Ph
e;	Me	H	Me
f;	H	Me	Me
g;	Me	Me	Me

The anhydro base (**13c**) reacted with bromine to give the bromoquinolinium bromide (characterised as the perchlorate salt) (**16**) which underwent smooth solvolysis to the acetate (**15l**), and hydrolysis to the hydroxy compound (**15k**).

The quinolinium oximes (**14m—p**) were obtained by the

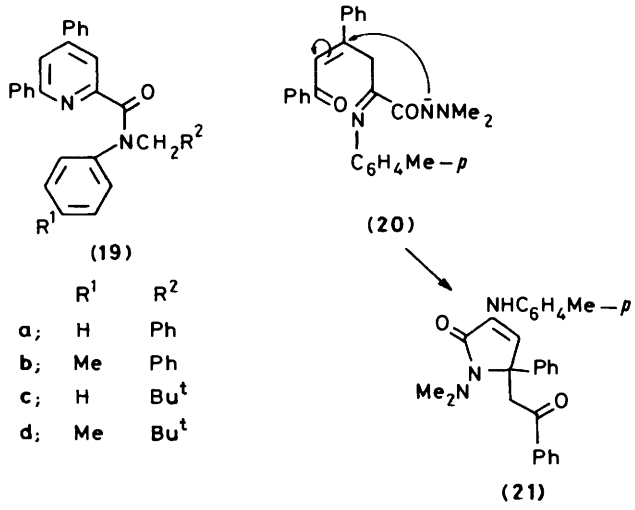


	R^1	R^2
a;	H	
b;	Me	
c;	H	*p*-Me
d;	H	H
e;	H	*p*-Cl
f;	H	*p*-Br
g;	Me	*p*-Me
h;	H	CH_2CO_2Et
i;	H	CH_2COPh
j;	Me	CH_2COPh
k;	OH	

	R^1	R^2
l;	OAc	
m;		*p*-Me
n;		H
o;		*p*-Cl
p;		*p*-Br
q;	Me	Me
r;	*p*-MeC_6H_4	H
s;	CH_2Ph	H
t;	*m*-MeC_6H_4	H
u;	*p*-ClC_6H_4	H
v;	Bu^t	H

Scheme.

reaction of nitrosyl chloride with the anhydro bases (**13m—p**) in ether (Table 5). Since the oximes (**14m—p**) were hygroscopic as chloride salts, they were converted into perchlorate salts. With the exception of (**14n**), these compounds crystallised with ethanol, as shown by the elemental analyses and ^1H and ^{13}C n.m.r. spectra (Tables 5, 6, and 11).



	R^1	R^2
a;	H	Ph
b;	Me	Ph
c;	H	Bu^t
d;	Me	Bu^t

Intramolecular Rearrangement.—When 1-aryl-2-(*N*-substituted carbamoyl)pyridinium salts (**7a—d**) were treated for 4 h with NaH in refluxing toluene,[3] 2-*N*-substituted-*N*-arylcarbamoyl)-4,6-diphenylpyridines (**19a—b**) were obtained in *ca.* 75% yield (Table 7). In their i.r. spectra, ν(C=O) appears at 1 650 cm^{-1}. The ^1H n.m.r. spectra (Table 8) show a characteristic singlet in the region δ 4—5 due to the methylene protons. However, attempts to rearrange the corresponding 2-(hydrazidocarbonyl)pyridinium salts were unsuccessful: only complex mixtures resulted when (**8a—g**) were treated with NaH in either toluene or DMF. When the rearrangement was attempted in THF, the temperature was insufficient to induce the rearrangement. Reaction of 2-(Dimethylhydrazidocarbonyl)-4,6-diphenyl-1-(*p*-tolyl)pyridinium tetrafluoroborate (**8g**) with NaH in THF gave the pyrrolinone (**21**). Compound (**21**) was characterised spectroscopically. The i.r. spectrum shows ν(NH) at 3 380 cm^{-1} and ν(C=O) at 1 680 (PhCO) and 1 650 cm^{-1} (NCO); the ^1H n.m.r. spectrum ($CDCl_3$) shows an AB pattern (*J* 16 Hz) at δ 3.2 and δ 4.7 due to the *gem*-CH_2 protons. The olefinic proton resonates at δ 6.5 and the aromatic protons at δ 7.2—7.8. In the ^{13}C n.m.r. spectrum the carbonyl carbons resonate at 196.5 (PhCO) and 164.8 (NCO) p.p.m., the methine carbon at 66.9 p.p.m., the methylene carbon at 43.6 p.p.m., the methyl carbons at 44.5 (NMe_2) and 20.5 p.p.m. (4-Me), and the aromatic and olefinic carbons in the region 139—108 p.p.m. The formation of (**21**) involves hydroxide ion addition to the pyridinium ring during work-up, followed by ring-opening to (**20**) and ring-closure to give the product (**21**).

Attempts to induce rearrangement of 8-substituted 1-aryl-5,6,7,8-tetrahydro-2,4-diphenylquinolinium salts (**11h—k**) failed: starting materials were recovered from the reaction of (**11h—j**) with NaH in solvents such as THF, toluene, DMF, and *o*-dichlorobenzene. The rearrangement of (**15k**) failed under basic conditions as decomposition occurred rapidly at pH 12 (25 °C), possibly due to C–C bond fission, as found previously for 2-hydroxymethylpyridinium cations.[9]

However, the quinolinium oximes (**14**) rearranged on heating at 100 °C with NaOEt and/or NaH in DMF for 6 h (Table 9). In the i.r. spectra of the rearrangement products (**17**) the expected ν(OH) was absent, probably owing to intramolecular hydrogen bonding with the heterocyclic nitrogen.

The ^1H n.m.r. spectra (60, 100 MHz) (Table 10) show an olefinic multiplet in the region δ 5.7—5.0, together with multiplets due to the C-5 and C-6 methylene protons, in a 3:1 ratio. The 300 MHz spectrum of (**17o**) showed a 1:2:1 ratio for the aliphatic protons, which could be assigned on irradiation of the signal due to 7-H as follows: δ 3.2—3.0 (6-H), 2.9—2.6 (5-H,

Table 1. Preparation of 1-aryl-2-(substituted carbamoyl or hydrazidocarbonyl)-4,6-diphenylpyridinium tetrafluoroborates (7) and (8)

Compd.	Method[a]	Yield (%)	M.p.[b] (°C)	Found (%) (Required) C	H	N	Formula
(7a)	A	60	222—224	70.0 (70.4)	5.0 (4.7)	5.1 (5.3)	$C_{31}H_{25}BF_4N_2O$
(7b)	A	61	210—211[c]	71.0 (70.8)	5.2 (5.2)	5.1 (5.4)	$C_{32}H_{27}BF_4N_2O$
(7c)	A	62	121—122	68.8 (68.5)	5.2 (5.7)	5.4 (5.5)	$C_{29}H_{29}BF_4N_2O$
(7d)	A	48	118—119	70.1 (69.0)	5.7 (5.9)	5.1 (5.4)	$C_{30}H_{31}BF_4N_2O$
(8a)	B	66	172—175	66.0 (65.8)	4.8 (4.8)	7.6 (7.7)	$C_{30}H_{24}BF_4N_3O{\cdot}H_2O$
(8b)	B	65	149—151	68.3 (68.5)	4.8 (4.8)	7.7 (7.7)	$C_{31}H_{26}BF_4N_3O$
(8c)	B	68	220—222	63.5 (63.9)	3.9 (4.1)	7.2 (7.5)	$C_{30}H_{23}BClF_4N_3O$
(8d)	B	73	276—280	71.0 (71.4)	4.5 (4.6)	6.6 (6.9)	$C_{36}H_{28}BF_4N_3O$
(8e)	C	70	185—187	65.1 (64.9)	5.1 (5.0)	8.5 (8.7)	$C_{26}H_{24}BF_4N_3O$
(8f)	B	74	161—163	65.0 (64.9)	5.2 (5.0)	8.7 (8.7)	$C_{26}H_{24}BF_4N_3O$
(8g)	B	75	142—145	62.8 (63.2)	5.3 (5.1)	7.9 (8.2)	$C_{27}H_{26}BF_4N_3O{\cdot}H_2O$

[a] See Experimental section. [b] Obtained as needles from absolute EtOH. [c] Needles from MeOH.

Table 2. ^{1}H N.m.r. spectra[a] of 1-aryl-2-(substituted carbamoyl or hydrazidocarbonyl)-4,6-diphenylpyridinium tetrafluoroborates (7) and (8)

Compd.	3-CH (1 H, d, *J* 2)	5-CH (1 H, d, *J* 2)	Ar-H m	H	m	H	N-H	Other-H NCH_2 (2 H, d, *J* 6)	Me (s)
(7a)	7.90	7.80	7.6—6.8	18			2.50	4.30	
(7b)	8.00	7.80	7.5—6.8	17			2.00	4.30	2.20[b]
(7c)	*c*	*c*	8.1—7.4	17			*c*	3.10	0.70[d]
(7d)	*c*	*c*	8.1—7.0	16			*c*	3.00	2.30[b], 0.70[d]
(8a)	8.30	8.15	7.5—7.3	18	6.25	2	2.45		
(8b)	8.33	8.15	7.5—7.3	17	6.30	2	2.40		2.24[b]
(8c)	8.25	8.18	7.5—7.3	17	6.30	2	2.40		
(8d)	8.31	8.20	7.6—7.3	22	6.30	2	2.45		
(8e)	8.35	8.15	7.5—7.2	14			2.48		2.95[b], 2.25[b]
(8f)	8.60	8.33	7.9—7.3	15			2.40		3.17[e]
(8g)	8.60	8.33	7.9—7.3	14			2.40		3.17[e], 2.29[b]

[a] Solutions in $CDCl_3$; δ in p.p.m.; *J* = coupling constant in Hz. [b] 3 H. [c] In the aromatic region. [d] 9 H. [e] 6 H.

6-H), and 2.0—1.7 (5-H). The ^{13}C n.m.r. spectra (Table 11) display triplets due C-5 and C-6 in the range 22—25 p.p.m., a doublet assigned to C-7 at *ca.* 78 p.p.m. and a singlet assigned to C-8 at *ca.* 89 p.p.m. All the aromatic carbons resonate in the range 116—156 p.p.m. In the mass spectra of (**17o**) and (**17p**) the parent ions were observed, the base and major peaks resulted from the loss of OH, H_2O and H_3O^+.

When the rearrangement of (**14m**) was attempted using 2.5—3 equiv. of NaH, the yield of (**17m**) decreased to 10%. However, from the reaction mixture together with decomposition products a fully aromatised quinoline (**18m**) was isolated by column chromatography (neutral alumina, hexane–CH_2Cl_2). The quinoline (**18m**) could be clearly identified by its mass spectrum, which showed the base peak at *m/z* 386 (M^+). Quinoline (**18**) could also be detected by t.l.c. (silica gel, CH_2Cl_2–hexane 80%), as the side-product of the reaction of (**14**) with 1 equiv. of base. The formation of this compound, together with the spectral data obtained for (**17**) help to confirm the proposed structures.

Experimental

M.p.s were obtained on a hot-stage apparatus, and are uncorrected. I.r. spectra utilised NaCl plates and a Perkin-Elmer 283B grating spectrophotometer (in $CHBr_3$). ^{1}H N.m.r. spectra were obtained on a Varian EM 360 L (60 MHz) and Nicolet NT-300 (300 MHz) spectrometers and ^{13}C n.m.r. spectra on JEOL JNM-FX100 (25.0 MHz) and Nicolet NT-300 (75.5 MHz) spectrometers. Mass spectra were recorded on an AEI MS 30 spectrometer.

The following compounds were prepared by literature methods: 2-ethoxycarbonyl-4,6-diphenylpyrylium tetrafluoroborate, m.p. 153—155 °C (lit.,[10] m.p. 155—157 °C); 1-phenyl-(**4a**) m.p. 184—186 °C (lit.,[11] m.p. 185—186 °C); 1-(*p*-tolyl)-(**4b**), m.p. 202—203 °C (lit.,[3] m.p. 202—203 °C); 1-(*p*-chlorophenyl)-(**4c**), m.p. 185—187 °C (lit.,[3] m.p. 185—187 °C), and *1-biphenyl-4-yl-2-ethoxycarbonyl-4,6-diphenylpyridiniumtetrafluoroborate* (**4d**) (90%), m.p. 182—184 °C (from EtOH) (Found: C, 70.8; H, 4.9; N, 2.5. $C_{32}H_{26}BF_4NO_2$ requires C, 70.7; H, 4.8; N, 2.6%); 1-phenyl-(**5a**), m.p. 150—151 °C (lit.,[11] m.p.

Table 3. Preparation of 8-[(*N*-substituted amino)methylene]-5,6,7,8-tetrahydrochromenylium trifluoromethanesulphonates (**12**)

Compd.	Crystal form[a]	M.p. (°C)	Yield (%)	Found (%) (Required) C	H	N	Formula
(**12q**)	Needles[b]	189	81	61.0 (61.1)	4.9 (4.9)	2.9 (2.9)	$C_{25}H_{24}F_3NO_4S$
(**12r**)	Prisms	278	83	65.2 (65.1)	4.8 (4.7)	2.5 (2.5)	$C_{30}H_{26}F_3NO_4S$
(**12s**)	Needles	215	89	65.1 (65.1)	4.8 (4.7)	2.5 (2.5)	$C_{30}H_{26}F_3NO_4S$
(**12t**)	Prisms	194	62	65.0 (65.1)	4.8 (4.7)	2.5 (2.5)	$C_{30}H_{26}F_3NO_4S$
(**12u**)	Prisms	295	51	60.5 (60.7)	4.1 (4.1)	2.4 (2.4)	$C_{29}H_{23}ClF_3NO_4S$
(**12v**)	Needles	194	87	62.5 (62.4)	5.5 (5.4)	2.7 (2.7)	$C_{27}H_{28}F_3NO_4S$

[a] Ethanol as recrystallisation solvent. [b] Ac_2O as recrystallisation solvent.

Table 4. ^1H N.m.r. spectra[a] of 8-(*N*-substituted aminomethylene)-5,6,7,8-tetrahydrochromenylium trifluoromethanesulphonates (**12**)

Compd.	3-CH (1 H, s)	Ar-H (m)	Ar-H H	Olefinic-H (1 H, s)	5,7-CH_2 (4 H, m)	6-CH_2 (2 H, m)	Me or CH_2 (s)	Me or CH_2 H
(**12q**)	8.17	8.0—7.2	10	6.95	3.0—2.5	2.0—1.5	3.50	6
(**12r**)	8.70	8.1—7.1	14	*b*	3.1—2.6	2.2—1.6	2.40	3
(**12s**)	8.20	7.8—7.2	15	7.05	3.0—2.4	2.2—1.6	4.83	2
(**12t**)	8.70	8.1—7.0	14	*b*	3.1—2.6	2.3—1.7	2.43	3
(**12u**)	8.65	8.1—7.0	14	*b*	3.2—2.4	2.3—1.6		
(**12v**)	8.40	7.8—7.1	10	6.97	2.9—2.3	2.0—1.5	1.53	9

[a] Solutions in $CDCl_3$–TFA; δ in p.p.m. [b] Signal embedded in the aromatic protons region.

Table 5. Preparation of 1-aryl-5,6,7,8-tetrahydro-8-oximino-2,4-diphenylquinolinium perchlorates (**14**)

Compd.	Yield (%)	M.p.[a] (°C)	Found (%) (Required) C	H	N	Formula
(**14m**)	59	150—152	65.6 (65.4)	5.6 (5.7)	5.4 (5.1)	$C_{28}H_{25}ClN_2O_5$ EtOH[b]
(**14n**)	41	149—152	65.9 (66.0)	4.8 (4.7)	5.7 (5.7)	$C_{27}H_{23}ClN_2O_5$
(**14o**)	60	162—165	60.8 (60.9)	4.9 (4.9)	4.7 (4.9)	$C_{27}H_{22}Cl_2N_2O_5$ EtOH[b]
(**14p**)	77	160—163	56.5 (56.5)	4.4 (4.6)	4.7 (4.5)	$C_{27}H_{22}BrClN_2O_5$ EtOH[b]

[a] All compounds recrystallised from EtOH as prisms. [b] Confirmed by ^1H n.m.r. spectrum.

Table 6. ^1H N.m.r. spectra[a] of 1-aryl-5,6,7,8-tetrahydro-8-oximino-2,4-diphenylquinolinium perchlorates (**14**)

Compd.	3-CH (1 H, s)	Ar-H (m)	Ar-H H	5,7-CH_2 (4 H, m)	6-CH_2 (2 H, m)	Other-H (3 H, s)
(**14m**)	7.75	7.7—6.8	14	3.1—2.6	2.2—1.6	2.23
(**14n**)[b]	7.70	7.6—7.0	15	3.0—2.4	2.1—1.6	
(**14o**)	7.83	7.7—7.1	14	3.1—2.4	2.2—1.7	
(**14p**)	8.05	7.9—7.0	14	3.4—2.7	2.4—1.7	

[a] Solution in $CDCl_3$–TFA; δ in p.p.m. [b] Solution in $CDCl_3$.

150 °C); 1-(*p*-tolyl)-(**5b**), m.p. 162—163 °C (lit.,[5] m.p. 162—163 °C); 1-(*p*-chlorophenyl)-(**5c**) m.p. 146—148 °C (lit.,[3] m.p. 146—148 °C); and 1-*biphenyl*-4-*yl*-4,6-*diphenylpyridinium*-2-*carboxylate* (**5d**) (80%), m.p. 157—160 °C (Found: C, 84.1; H, 4.7; N, 3.2. $C_{30}H_{21}NO_2$ requires C, 84.3; H, 4.9; N, 3.3%); 5,6,7,8-tetrahydro-2,4-diphenylchromenylium trifluoromethanesulphonate (**9a**), m.p. 185—187 °C (lit.,[5] 187 °C); 5,6,7,8-tetrahydro-8-methyl-2,4-diphenylchromenylium trifluoromethanesulphonate (**9b**), m.p. 127—130 °C (lit.,[6] m.p. 130—133 °C); 1-(*p*-tolyl)-(**10c**), m.p. 170—172 °C (lit.,[2] m.p. 171—173 °C); 1-

Table 7. Preparation of 2-(*N*-aryl-*N*-substituted carbamoyl)-4,6-diphenylpyridines (**19**)

Compd.	Yield (%)	M.p.[a] (°C)	Found (%) (Required) C	H	N	Formula
(**19a**)[b]	74	162—163[b]	84.1 (84.5)	5.7 (5.5)	6.1 (6.4)	$C_{31}H_{24}N_2O$
(**19b**)	77	146—147	84.3 (84.6)	5.6 (5.7)	5.9 (6.2)	$C_{32}H_{26}N_2O$
(**19c**)	80	135—136	82.5 (82.9)	6.3 (6.7)	6.8 (6.7)	$C_{29}H_{28}N_2O$
(**19d**)	70	131—132	82.7 (82.9)	6.7 (6.9)	6.3 (6.5)	$C_{30}H_{30}N_2O$

[a] Plates from MeOH. [b] Plates from absolute EtOH.

Table 8. ^{1}H N.m.r. spectra[a] of 2-(*N*-aryl-*N*-substituted carbamoyl)-4,6-diphenylpyridines (**19**)

Compd.	3-CH (1 H, d, *J* 2)	5-CH (1 H, d, *J* 2)	Ar-H (m)	Ar-H H	Other-H NCH_2 (2 H, s)	Other-H Me (s)	Other-H Me H
(**19a**)	7.90	7.70	7.6—6.9	20	5.15		
(**19b**)	7.80	7.70	7.5—7.0	19	5.15	2.20	3
(**19c**)	*b*	*b*	7.8—7.1	17	4.10	1.00	9
(**19d**)	*b*	*b*	7.7—7.0	16	4.00	2.20	3
						0.90	9

[a] Solutions in $CDCl_3$; δ in p.p.m.; *J* = coupling constant in Hz. [b] With the other Ar-H.

Table 9. Preparation of 8-(*N*-aryl-*N*-hydroxyamino)-5,6-dihydro-2,4-diphenylquinolines (**17**)

Compd.	Yield (%)	M.p.[a] (°C)	Found (%) (Required) C	H	N	Formula
(**17m**)	56	162—164	83.1 (83.1)	6.0 (6.0)	6.9 (6.9)	$C_{28}H_{24}N_2O$
(**17n**)	36	260—262	82.9 (83.0)	5.7 (5.7)	7.2 (7.2)	$C_{27}H_{22}N_2O$
(**17o**)	58	282—284	76.1 (76.3)	5.0 (5.0)	6.6 (6.6)	$C_{27}H_{21}ClN_2O$
(**17p**)	46	274—276	69.0 (69.1)	4.6 (4.5)	6.0 (6.0)	$C_{27}H_{21}BrN_2O$

[a] All compounds recrystallised from CH_2Cl_2–EtOH as prisms.

Table 10. ^{1}H N.m.r. spectra[a] of 8-(*N*-aryl-*N*-hydroxyamino)-5,6-dihydro-2,4-diphenylquinolines (**17**)

Compd.	Ar-H (m)	Ar-H H	7-CH (1 H, m)	5,6-CH_2CH_2 (3 H, m)	5,6-CH_2CH_2 (1 H, m)
(**17m**)[b]	8.0—6.5	15	5.3—4.9	3.4—2.5	2.1—1.5
(**17n**)	8.1—6.6	16	5.7—5.3	3.4—2.5	2.3—1.6
(**17o**)	7.9—6.6	15	5.3—5.0	3.4—2.4[c]	2.2—1.6[c]
(**17p**)	8.0—6.4	15	5.3—5.0	3.3—2.4	2.2—1.5

[a] Solutions in $CDCl_3$–TFA; δ in p.p.m. [b] Solution in $CDCl_3$; Me (2.16, 3*H*, s). [c] 300 MHz ^{1}H n.m.r.: δ 3.2—3.0 (1 H, m), 2.9—2.6 (2 H, m), and 2.0—1.7 (1 H, m).

phenyl-(**10d**), m.p. 204—206 °C (lit.,[2] m.p. 203—205 °C); 1-(*p*-chlorophenyl)-(**10e**), m.p. 147—148 °C (lit.,[2] m.p. 146—148 °C), and 1-(*p*-bromophenyl)-5,6,7,8-tetrahydro-2,4-diphenylquinolinium trifluoromethanesulphonate (**10f**), m.p. 158—159 °C (lit.,[2] m.p. 156—158 °C); 1-(*p*-tolyl)-(**13c**), m.p. 131—133 °C (lit.,[2] m.p. 130—132 °C); 1-phenyl-(**13d**), m.p. 109—110 °C (lit.,[2] m.p. 110—112 °C); 1-(*p*-chlorophenyl)-(**13e**), m.p. 149—150 °C (lit.,[2] m.p. 146—148 °C); and 1-(*p*-bromophenyl)-1,5,6,7-tetrahydro-2,4-diphenylquinoline (**13f**), m.p. 125—126 °C (lit.,[2] m.p. 125—127 °C).

Preparation of 1-*Aryl*-2-(N-*substituted carbamoyl*)-(**7**) *and* 1-*Aryl* 2-(*substituted hydrazidocarbonyl*)-4,6-*diphenylpyridinium Tetrafluoroborate* (**8**).—*Method A.* Thionyl chloride (18 mmol), 1-aryl-4,6-diphenylpyridinium-2-carboxylate (**4**) (6 mmol), and CH_2Cl_2 (15 ml) were refluxed for 2 h. The CH_2Cl_2 and an excess of thionyl chloride were removed under reduced pressure (50 °C/20 mmHg). To the residue dissolved in CH_2Cl_2 (10 ml) was added the amine (18 mmol) and the mixture was refluxed for 3 h. The solution was evaporated (50 °C/20 mmHg) and the residue washed successively with water (50 ml) and Et_2O (50 ml). The resultant gum was dissolved in ethanol (15 ml) and tetrafluoroboric acid (40%, 10 mmol) added to form, after cooling, the *carbamoyl tetrafluoroborate* (**7**) (Table 1).

Table 11. ^{13}C N.m.r. chemical shifts[a] of 1-aryl-5,6,7,8-tetrahydro-8-oximino-2,4-diphenylquinolinium perchlorates (**14**) and 8-(*N*-aryl-*N*-hydroxyamino)-5,6-dihydro-2,4-diphenylquinolines (**17**).

Compd.	Aromatic-C	C-5 (t)	C-6 (t)	C-7	C-8 (s)	Me (q)
(**14m**)[b]	157.8—127.6	24.3	19.5	27.5 (t)	146.5	19.5
(**14n**)[b]	157.8—128.0	24.2	19.4	27.6 (t)	146.7	
(**14o**)[b]	158.6—128.5	24.4	19.4	27.6 (t)	146.3	
(**14p**)[b]	159.2—124.4	24.6	19.7	27.8 (t)	146.3	
(**17m**)[c]	154.6—116.3	24.8	22.9	78.9 (d)	89.1	20.6
(**17o**)[c]	154.5—118.0	24.5	22.4	77.8 (d)	88.9	
(**17p**)[c]	156.4—117.8	24.5	22.4	77.8 (d)	88.9	

[a] In $CDCl_3$–TFA, with $CDCl_3$ (77.0 p.p.m.) as reference. [b] Assignments of C-5 and C-7 could be interchanged. Assignment of C-8 was based on the low intensity of this signal. [c] Assignments of C-5 and C-6 could be interchanged.

Method B. The substituted hydrazine (18 mmol) was added to the residue dissolved in CH_2Cl_2 as in Method A, and the mixture stirred at 0 °C for 1 h; work-up as above gave the *hydrazidocarbonyl salts* (**8a**—**d**, **f**, and **g**) (Table 1).

Method C. The residue (**6b**) in CH_2Cl_2 (10 ml) was added dropwise over 1 h to a stirred solution at 0 °C of methylhydrazine (18 mmol) in CH_2Cl_2 (10 ml); work-up as above gave (**8e**) (Table 1).

1,5,6,7-*Tetrahydro*-8-*methyl*-2,4-*diphenyl*-1-(p-*tolyl*)*quinoline* (**13g**).—5,6,7,8-Tetrahydro-8-methyl-2,4-diphenylchromenylium trifluoromethanesulphonate (**9b**) (6.6 g, 14.5 mmol), CH_2Cl_2 (50 ml), *p*-toluidine (1.6 g, 14.5 mmol), and Et_3N (1.5 g, 14.5 mmol) were refluxed for 1 h; AcOH (1.7 g, 29 mmol) was added and the solution washed with water (2 × 25 ml), dried ($MgSO_4$), and evaporated at 50 °C/5 mmHg. The resultant gum was triturated with Et_2O to give the crude triflate salt (**10g**) (5.1 g, 65%). To a stirred ethanol solution (20 ml) of crude 5,6,7,8-tetrahydro-8-methyl-2,4-diphenyl-1-(*p*-tolyl)quinolinium triflate (**10g**) (1.3 g, 2.4 mmol) was added NaH (97%, 0.12 g, 4.8 mmol). The *title compound* precipitated out after 15 min, and was filtered off and washed with H_2O to yield 0.6 g (65%) as prisms, m.p. 143 °C (Found: C, 89.3; H, 7.0; N, 3.5. $C_{29}H_{27}N$ requires C, 89.4; H, 7.0; N, 3.6%); δ($CDCl_3$) 7.8—6.6 (14 H, m), 6.46 (1 H, s), 2.13 (3 H, s), 1.93 (3 H, s), and 2.7—1.4 (6 H, m); $\nu_{max.}$($CHBr_3$) 1 600s, 1 500s, 1 440s, 1 230s, 800s, and 760s. The corresponding *perchlorate salt* was obtained by addition of $HClO_4$ (60%) to an ethanolic solution of (**13g**) as prisms (90%), m.p. 184 °C (Found: C, 71.0; H, 5.9; N, 2.8. $C_{29}H_{28}ClNO_4$ requires C, 71.1; H, 5.8; N, 2.9%); δ($CDCl_3$) 8.0—6.8 (15 H, m), 3.5—2.6 (3 H, m), 2.26 (3 H, s), 2.2—1.4 (4 H, m), and 1.13 (3 H, d, *J* 7 Hz); $\nu_{max.}$($CHBr_3$) 1 610s, 1 600s, and 1 080b.

8-(*Ethoxycarbonylmethyl*)-5,6,7,8-*tetrahydro*-2,4-*diphenyl*-1-(p-*tolyl*)*quinolinium Perchlorate* (**11h**).—1,5,6,7-Tetrahydro-2,4-diphenyl-1-(*p*-tolyl)quinoline (**13c**) (1 g, 2.7 mmol), $BrCH_2CO_2Et$ (0.7 g, 4.0 mmol), and THF (10 ml) were refluxed for 5 min. Et_2O (50 ml) was added and the resulting precipitate collected and dissolved in EtOH (10 ml). Addition of $HClO_4$ (60%; 1 ml) gave the *perchlorate* which, after washing with water (20 ml) formed needles (1.0 g, 67%), m.p. 209 °C (Found: C, 68.4; H, 5.8; N, 2.5. $C_{32}H_{32}ClNO_6$ requires C, 68.4; H, 5.8; N, 2.5%); δ($CDCl_3$) 7.9—6.7 (15 H, m), 3.86 (2 H, q, *J* 6 Hz), 3.8—3.5 (1 H, m), 3.2—2.6 (4 H, m), 2.23 (3 H, s), 2.2—1.4 (2 H, m), and 1.06 (3 H, t, *J* 6); $\nu_{max.}$($CHBr_3$) 1 730s, 1 610s, and 1 080br.

5,6,7,8-*Tetrahydro*-8-*phenacyl*-2,4-*diphenyl*-1-(p-*tolyl*)*quinolinium Perchlorate* (**11i**). This compound was prepared similarly (with $BrCH_2COPh$ as the nucleophile) as prisms (73%), m.p. 224 °C (Found: C, 72.6; H, 5.4; N, 2.3. $C_{36}H_{32}ClNO_5$ requires C, 72.8; H, 5.4; N, 2.4%); δ ($CDCl_3$–TFA) 8.0—6.5 (20 H, m), 4.3—3.9 (1 H, m), 3.6—3.2 (2 H, m), 3.2—2.7 (4 H, m), 2.4—1.6 (2 H, m), and 2.20 (3 H, s); $\nu_{max.}$($CHBr_3$) 1 670s, 1 600s, and 1 080br.

5,6,7,8-*Tetrahydro*-8-*methyl*-8-*phenacyl*-2,4-*diphenyl*-1-(p-*tolyl*)*quinolinium Perchlorate* (**11j**).—1,5,6,7-Tetrahydro-8-methyl-2,4-diphenyl-1-(*p*-tolyl)quinoline (**13g**) (0.5 g, 1.3 mmol), $BrCH_2COPh$ (0.38 g, 1.9 mmol), and THF (10 ml) were refluxed for 5 h; Et_2O (50 ml) was added and the precipitate collected. The work-up procedure described above gave the *title compound* as prisms (0.55 g, 70%), m.p. 141 °C (Found: C, 72.8; H, 5.7; N, 2.3. $C_{37}H_{34}ClNO_5$ requires C, 73.1; H, 5.7; N, 2.3%); δ ($CDCl_3$–TFA) 8.0—6.2 (20 H, m), 3.7—1.0 (8 H, m), 2.20 (3 H, s), and 1.70 (3 H, s); $\nu_{max.}$($CHBr_3$) 1 670s, 1 610s, and 1 080br.

8-*Bromo*-5,6,7,8-*tetrahydro*-2,4-*diphenyl*-1-(p-*tolyl*)*quinolinium Perchlorate* (**16**).—To a stirred solution of 1,5,6,7-tetrahydro-2,4-diphenyl-1-(*p*-tolyl)quinoline (**13c**) (2 g, 5.3 mmol) in Et_2O (400 ml) was added dropwise excess Br_2 until the solution turned yellow. The yellow precipitate was filtered off dissolved in EtOH (10 ml) and $HClO_4$ (60%; 2 ml) added to the solution. The *title compound* precipitated and was filtered off and washed with water (20 ml) (2.4 g, 81%), prisms, m.p. 176 °C (Found: C, 60.7; H, 4.6; N, 2.5. $C_{28}H_{25}BrClNO_4$ requires C, 60.6; H, 4.6; N, 2.5%); δ ($CDCl_3$–TFA) 8.1—6.9 (15 H, m), 5.20 (1 H, m), 3.4—2.9 (4 H, m), 2.7—1.7 (2 H, m), and 2.30 (3 H, s); $\nu_{max.}$($CHBr_3$) 1 610s and 1 080br.

8-*Acetoxy*-5,6,7,8-*tetrahydro*-2,4-*diphenyl*-1-(p-*tolyl*)-*quinolinium Perchlorate* (**15l**).—NaOAc (0.14 g, 1.7 mmol) was added to8-bromo-5,6,7,8-tetrahydro-2,4-diphenyl-1-(*p*-tolyl)quinolinium bromide (**16**) (0.5 g, 1.1 mmol) in AcOH (10 ml). The mixture was refluxed for 1 h and $HClO_4$ (60%, 0.5 ml) was added, followed by water (10 ml). The precipitate was filtered off, washed with water (10 ml), and recrystallised from PhMe–Et_2O to give the *title compound* as prisms (0.35 g, 60%), m.p. 145 °C (Found: C, 67.5; H, 5.3; N, 2.6. $C_{30}H_{28}ClNO_6$ requires C, 67.5; H, 5.3; N, 2.6%); δ($CDCl_3$) 8.0—7.0 (15 H, m), 5.93 (1 H, m), 3.3—2.8 (4 H, m), 2.6—1.5 (2 H, m), 2.26 (3 H, s), and 1.86 (3 H, s); $\nu_{max.}$($CHBr_3$) 1 735 s, 1 610s, and 1 080br.

8-*Hydroxy*-5,6,7,8-*tetrahydro*-2,4-*diphenyl*-1-(p-*tolyl*)-*quinolinium Tetrafluoroborate* (**15k**).—8-Bromo-5,6,7,8-tetrahydro-2,4-diphenyl-1-(*p*-tolyl)quinolinium bromide (**16**) (0.5 g, 1.1 mmol) was refluxed in water (50 ml) for 24 h after which HBF_4 (40%, 0.8 ml) was added. The precipitate was filtered off, washed with water (10 ml), and recrystallised from PhMe–Et_2O to give the *title compound* as prisms (0.39 g, 74%), m.p. 135 °C (decomp.) (Found: C, 70.1; H, 5.5; N, 2.9. $C_{28}H_{26}BF_4NO$ requires C, 70.2; H, 5.5; N, 2.9%); δ($CDCl_3$) 7.8—6.8 (15 H, m), 4.70 (1 H, m), 3.2—2.6 (4 H, m), 2.5—1.4 (2

H, m), and 2.23 (3 H, s); $\nu_{max.}$($CHBr_3$) 3 500br, 1 615s, and 1 050br.

8-[(N,N-*Dimethylamino*)*methylene*]-5,6,7,8-*tetrahydro*-2,4-*diphenylchromenylium Trifluoromethanesulphonate* (**12a**).—5,6,7,8-Tetrahydro-2,4-diphenylchromenylium trifluoromethanesulphonate (**9a**) (1 g, 2.3 mmol) was refluxed in a mixture of DMF (0.6 ml) and Ac_2O (4 ml) for 15 min. Et_2O (50 ml) was then added and the precipitate filtered off to give the *title compound*; this was recrystallised from Ac_2O to give needles (0.9 g, 81%), m.p. 189 °C (Found: C, 61.0; H, 4.9; N, 2.9. $C_{25}H_{24}F_3NO_4S$ requires C, 61.1; H, 4.9; N, 2.9%); δ($CDCl_3$–TFA) 8.17 (1 H, s), 8.0—7.2 (10 H, m), 6.95 (1 H, s), 3.50 (6 H, s), and 3.0—1.5 (6 H, m); $\nu_{max.}$($CHBr_3$) 1 615s, 1 250s, and 1 020m.

5,6,7,8-*Tetrahydro*-2,4-*diphenyl*-8-[(N-*substituted amino*)-*methylene*]*chromenylium Trifluoromethanesulphonates* (**12r–v**).—To a solution of the 8-(dimethylamino)methylene compound (**12g**) (1 g, 2.9 mmol) in CH_2Cl_2 (20 ml) was added the corresponding amine (1 equiv.) and Et_3N (1 equiv.). The mixture was stirred at 20 °C for 8—24 h after which AcOH (1.5 equiv.) was added. The solvent was removed (80 °C/5 mmHg) to leave a dark brown residue which when triturated with Et_2O (10 ml), H_2O (5 ml) and recrystallised from EtOH gave the chromenylium salt.

Preparation of the Quinolinium Oximes (**14**).—Into a stirred solution of 1-aryl-1,5,6,7-tetrahydro-2,4-diphenylquinoline (**13**) (1 g) in Et_2O (100—150 ml) was bubbled NOCl gas (generated from $NaNO_2$ and HCl) until the red colour completely disappeared. The resulting yellow precipitate was filtered off and dissolved in a minimum of EtOH; addition of $NaClO_4$ (50%, 1.3 ml) gave the quinolinium oxime which precipitated on stirring (Table 5).

2-(N-*Aryl*-N-*substituted carbamoyl*)-4,6-*diphenylpyridines* (**19a—d**).—Sodium hydride (97%, 0.15 g, 6 mmol) was added to the 1-aryl-2-(*N*-substituted carbamoyl)-4,6-diphenylpyridinium tetrafluoroborate (**7**) (3 mmol) in toluene (15 ml), and the mixture refluxed for 4 h. The solvent was removed (60 °C/10 mmHg) and the resulting solid washed with water (50 ml), filtered off, and recrystallised (Table 7).

5-*Benzoylmethyl*-1-(N,N-*dimethylamino*)-5-*phenyl*-3-(p-*tolylamino*)-5H-*pyrrol*-2(1H)-*one* (**21**).—2-(*N,N*-Dimethylhydrazidocarbonyl)-4,6-diphenyl-1-(*p*-tolyl)pyridinium tetrafluoroborate (**8g**) (0.5 g, 1 mmol) and sodium hydride (97%; 0.050 g, 2 mmol) were refluxed in THF (10 ml) for 4 h. The solvent was then removed (50 °C/10 mmHg) and the resultant solid washed with water (20 ml), filtered off (0.35 g, 73%), and recrystallised from MeCN to give prisms; δ_H($CDCl_3$) 7.9—7.2 (14 H, m), 4.70 (1 H, AB, *J* 16 Hz), 3.2 (1 H, AB, *J* 16 Hz), 2.75 (6 H, s), and 2.22 (3 H, s); δ_C 196.5 (s), 164.8 (s), 139—108 (Ar – *C* + *C*=), 66.9 (s), 44.5 (q), 43.6 (t), and 20.5 (q); $\nu_{max.}$($CHBr_3$) 3 380s, 1 680s, and 1 650s.

Preparation of 8-[*Aryl*(*hydroxy*)*amino*]-5,6-*dihydro*-2,4-*diphenylquinolines* (**17m—p**).—*Method A.* NaH (97%; 2.1 mmol) was added to the quinolinium oxime (**14**) (2.0 mmol) in DMF (20 ml) and the mixture heated at 100 °C for 6 h. Removal of the solvent 60 °C/2 mmHg) gave a brown residue which was washed with water (50 ml) and Et_2O (25 ml), and the resultant solid recrystallised from CH_2Cl_2–EtOH to give the corresponding title compound (**17m—p**) (Table 9).

Method B. Reaction of (**14m**) (1 g, 1.8 mmol) with NaH (97%; 0.13 g, 5.25 mmol) under the above conditions gave (**17m**) (75 mg, 10%). The ethereal extracts (2 × 25 ml) were dried ($MgSO_4$), ether was removed (25 °C/20 mmHg), and the brown residue passed through a column (neutral alumina, hexane–CH_2Cl_2) to give 2,4-*diphenyl*-8-p-*tolylaminequinoline* (**18m**) (110 mg, 16%) yellow needles (CH_2Cl_2–EtOH), m.p. 131—132 °C (Found: C, 86.7; H, 5.8; N, 7.1. $C_{28}H_{22}N_2$ requires C, 87.1; H, 5.7; N, 7.3%); δ_H($CDCl_3$) 8.70 (1 H, s, NH), 8.6—8.3 (2 H, m) 8.10 (1 H, s), 7.9—7.3 (17 H, m), and 2.40 (3 H, s); δ_C ($CDCl_3$; 75.5 MHz) 153.4 (s), 149.3 (s), 141.3 (s), 139.4 (s), 139.3 (s), 138.8 (s), 138.4 (s), 131.9 (d), 129.8 (d), 129.5 (d), 129.1 (d), 128.7 (d), 128.4 (d), 128.2 (d), 127.3 (d), 127.0 (d), 126.2 (s), 121.0 (d), 119.5 (d), 113.9 (d), 107.3 (d), and 20.8 (q); $\nu_{max.}$($CHBr_3$). 3 340w and 1 570m,br. High resolution m.s. (M^+): Found, *m/z* 386.1786; Calc. for $C_{28}H_{22}N_2$: *m/z*, 386.1783.

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