

Nucleophilic Displacements of *N*-Aryl and Heteroaryl Groups. Part 3.¹ Pyrylium-mediated Synthesis of Unsymmetrical Diarylamines from Anilines

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2-Ethoxycarbonyl-4,6-diphenylpyrylium salts (1) reacted with various ring-substituted anilines to give the corresponding pyridinium salts (2) (average yield 90%); these were hydrolysed to the pyridinium betaines (3) (75%) and treated with thionyl chloride followed by an aniline to give the amides (4) (70%). Refluxing in toluene with sodium hydride for 12 h transfers intramolecularly the 1-aryl group of the pyridinium salt (4) to the nitrogen of the amide. Aqueous work-up cleaves (6) and the diarylamine is purified by sublimation (60%) (overall yield *ca.* 30%).

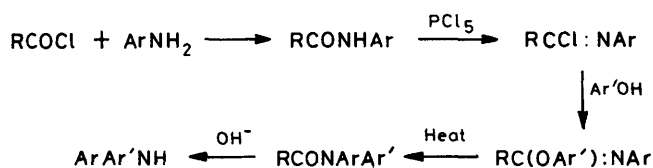
Diarylamines have been prepared from anilines by copper-catalysed condensation with an aryl halide, the Ullmann reaction,^{2a} typically in pentyl alcohol at 130 °C in the presence of a base to remove the liberated hydrogen halide. The yields of diarylamines are strongly dependent on the nature of the ring substituents. Activating groups in the aryl halide give rise to good yields (80–90%) whilst their absence leads to greatly reduced yields as does low nucleophilicity of the aniline as caused by electron-withdrawing *meta*- or *para*- or any *ortho*-substituents.^{2b}

For diarylamines that contain no nitro or carboxy groups, the Goldberg reaction^{3,4} can be used; the aniline is first converted into an *N*-acylaniline and then treated with aryl halides in nitrobenzene at 180 °C and finally hydrolysed.

Diarylamines also result by treating an aniline with a phenol⁵ at 250 °C with antimony trichloride as a catalyst. Nitrobenzene and phenylmagnesium bromide were reported to give diphenylamine (45%).⁶ Certain symmetrical diarylamines are formed by pyrolysis of equimolar amounts of the aniline and its hydrochloride.⁵

Another method of preparing diarylamines is the Smiles rearrangement of amides,⁷ but this requires a strongly electron-withdrawing group *ortho* or *para* to the displaced group. All diarylamines prepared by this method contain at least one nitro substituent. The amide is refluxed in ethanolic sodium ethoxide for 15–20 min, and yields are generally 60–80% depending on the degree of activation.⁹

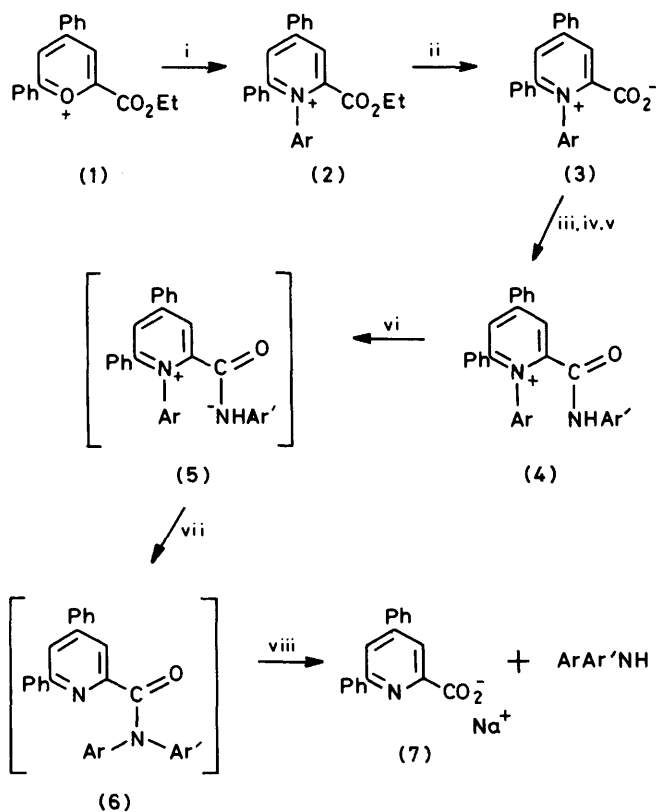
The five-step synthesis of diarylamines from anilines *via* the Chapman rearrangement of imino ethers (Scheme 1)^{8,10,11} gives overall yields of *ca.* 30%. The anilines and acid chloride form the amides (75%)¹² which are converted by phosphorus pentachloride into imino halides (70%).¹³ Treatment with a substituted phenol forms the imino ethers (70%),¹⁴ which undergo thermolysis (200–300 °C) to the amides and on hydrolysis give diarylamines (85–90%). Electron-withdrawing groups in the displaced aryl nucleus enhance the rearrangement, whereas reduced yields are obtained if electron-donating substituents are present.⁸



Scheme 1. Preparation of diarylamines by the Chapman rearrangement

None of the aforementioned methods constitutes a general preparation of diarylamines containing thermally sensitive but no activating substituents.

Our search for a mild method for the conversion of anilines into other functionalities *via* pyridinium salts has demonstrated¹⁵ that, whereas intermolecular nucleophilic displacements of 1-aryl substituents occurs only at high temperature, if at all, if a suitable nucleophilic centre is built into the molecule intramolecular nucleophilic displacement can occur under relatively mild conditions. Such displaced aryl groups need not contain activating substituents.^{1,15} We now describe a



(For designations of Ar and Ar' in (2), (3), (4), (5), (6), and (8) see Tables 1, 3, 5, and 7)

Scheme. Reagents: i, ArNH₂; ii, NaOH-H₂O; iii, SOCl₂; iv, Ar'NH₂; v, HBF₄; vi, PhMe-NaH; vii, Heat; viii, H₂O

Table 1. Preparation of 1-aryl-2-ethoxycarbonyl-4,6-diphenylpyridinium salts

Compd.	1-Substituent	Anion	Solvent	Time (h)	Yield (%)	M.p. ^a (°C)	Found (%) (Required %)			Molecular formula
							C	H	N	
(2a)	Ph	BF ₄	CH ₂ Cl ₂	2	95	184—186 ^b				
(2a)	Ph	CF ₃ SO ₃	CH ₂ Cl ₂	3	90	160—162	61.2 (61.2)	4.1 (4.2)	2.6 (2.7)	C ₂₇ H ₂₂ F ₃ NO ₅ S
(2b)	4-MeC ₆ H ₄	BF ₄	CH ₂ Cl ₂	2	93	202—203	67.3 (67.0)	5.0 (4.8)	2.9 (2.9)	C ₂₈ H ₂₄ BF ₄ NO ₂
(2b)	4-MeC ₆ H ₄	CF ₃ SO ₃	CH ₂ Cl ₂	4	94	176—178	59.8 (59.7)	4.3 (4.4)	2.5 (2.6)	C ₂₈ H ₂₄ F ₃ NO ₅ S
(2c)	4-ClC ₆ H ₄	BF ₄	CH ₂ Cl ₂	3	77	185—187	62.2 (62.2)	4.0 (4.2)	2.7 (2.8)	C ₂₆ H ₂₁ BClF ₄ NO ₂
(2d)	4-MeOC ₆ H ₄	BF ₄	CH ₂ Cl ₂	3	92	176—177	64.9 (65.2)	4.9 (4.8)	2.8 (2.8)	C ₂₇ H ₂₄ BF ₄ NO ₃
(2e)	4-NO ₂ C ₆ H ₄	BF ₄	EtOH	8	84	189—190	60.6 (60.9)	4.1 (4.1)	5.4 (5.5)	C ₂₆ H ₂₁ BF ₄ N ₂ O ₄

^a Recrystallised from 95% EtOH. ^b Lit.,¹⁸ m.p. 185—186 °C.

Table 2. ¹H N.m.r.^a of 1-aryl-2-ethoxycarbonyl-4,6-diphenylpyridinium salts

Compd.	1-Substituent	3-CH (1 H, d, J 2)	5-CH (1 H, d, J 2)	4,6-Diphenyl (10 H, m)	Aromatic protons of 1-substituent (m)				O ⁻ CH ₂ CH ₃ (2 H, q, J 7)	O ⁻ CH ₂ CH ₃ (3 H, t, J 7)	Other (3 H, s)
					δ	H	δ	H			
(2a)	Ph	8.30	8.10	7.25—7.65	7.80	3	6.90	2	4.15	1.05	—
(2b)	4-MeC ₆ H ₄	8.35	8.05	7.20—7.60	7.80	2	6.90	2	4.10	0.95	2.22
(2c)	4-ClC ₆ H ₄	8.45	8.05	7.25—7.60	7.80	2	7.10	2	4.20	1.05	—
(2d)	4-MeOC ₆ H ₄	8.40	8.15	7.15—7.60	7.80	2	6.75	2	4.20	1.10	3.78
(2e)	4-NO ₂ C ₆ H ₄	8.30	8.15	7.10—7.45	7.75	2	7.05	2	4.30	1.15	—

^a δ(CDCl₃), J in Hz.

Table 3. Preparation of 1-aryl-4,6-diphenylpyridinium-2-carboxylates

Compd.	1-Substituent	Yield ^a (%)	M.p. (°C)	Found (%)			Molecular formula	Required (%)		
				C	H	N		C	H	N
(3a)	Ph	85	150—151 ^b	81.6	4.9	3.8	C ₂₄ H ₁₇ NO ₂	82.0	4.9	4.0
(3b)	4-MeC ₆ H ₄	86	162—163	82.2	5.2	3.8	C ₂₅ H ₁₉ NO ₂	81.8	5.1	3.6
(3c)	4-ClC ₆ H ₄	73	146—148	71.1	4.5	3.5	C ₂₄ H ₁₆ ClNO ₂ ·H ₂ O	71.4	4.5	3.5
(3d)	4-MeOC ₆ H ₄	69	141—142	71.4	4.9	3.1	C ₂₅ H ₁₉ NO ₃ ·2H ₂ O	71.6	4.5	3.3
(3e)	4-NO ₂ C ₆ H ₄	68	155—156 ^c							

^a Reactions carried out in water at 25 °C for 24 h. ^b Lit.,¹⁸ m.p. 150 °C. ^c Hygroscopic, characterised from spectral data.

method of preparing diarylamines from anilines *via* 1-arylpyridinium salts which have an amide functionality at the 2-position.

Preparation of 1-Aryl-2-ethoxycarbonyl-4,6-diphenylpyridinium Salts (2) and the Corresponding Betaines (3).—2-Ethoxycarbonyl-4,6-diphenylpyridinium (1) tetrafluoroborate¹⁶ and trifluoromethanesulphonate¹⁷ were prepared as previously described from benzylideneacetophenone and ethyl pyruvate. The pyridinium salts (1) smoothly reacted with a series of ring-substituted anilines in dichloromethane to give¹⁸ the corresponding pyridinium salts (2a—e) (ca. 90%) (Table 1). Basic hydrolysis of (2a—e) with aqueous sodium hydroxide at ambient temperature gave¹⁸ the corresponding betaines (3a—e) (ca. 75%) (Table 3).

Preparation of 1-Aryl-2-(N-arylcarbamoyl)-4,6-diphenylpyridinium Salts (4).—Initial attempts to prepare the pyridinium amides (4) by reaction of 2-ethoxycarbonylpyridinium salts (2) with aniline and also in the presence of bases such as

ethoxide failed. However pyridinium betaines (3a—d) refluxed in dichloromethane with thionyl chloride and pyridine gave the acid chloride, converted *in situ* by an added aniline into the 2-(N-arylcarbamoyl)pyridinium salts (4a—i) (ca. 70%) (Table 5).

Intramolecular Rearrangement of 2-(N-Arylcarbamoyl)pyridinium Salts (4).—Initially, 2-(N-arylcarbamoyl)pyridinium salts (4) were treated with base at 25 °C in attempts to form the amido anion (5) as an isolable zwitterion; experiments using bases such as hydride and ethoxide in tetrahydrofuran or ethanol indicated, however, that complete conversion into the amido anion did not occur. Amide anions are frequently difficult to isolate.¹⁹ However reaction in refluxing toluene with sodium hydride forms the amide anion (5) *in situ* and causes spontaneous rearrangement into the pyridine derivative (6). Removal of the solvent and addition of water results in cleavage of (6) into the sodium salt of 2,4-diphenylpicolinic acid (7) and the diarylamine (8). The acid (7) was obtained on acidification. The diarylamine (8) was

Table 4. ^1H N.m.r.^a of 1-aryl-4,6-diphenylpyridinium-2-carboxylates

Compd.	1-Substituent	3-CH (1 H, d, <i>J</i> 2)	5-CH (1 H, d, <i>J</i> 2)	4,6-Diphenyl (10 H, m)	Aromatic protons of 1-substituent (m)				Other (3 H, s)
					δ	H	δ	H	
(3a)	Ph	8.15	7.94	7.30—7.42	7.64	3	7.05	2	—
(3b)	4-MeC ₆ H ₄	8.18	7.90	7.30—7.53	7.66	2	7.05	2	2.26
(3c)	4-ClC ₆ H ₄	8.08	7.87	7.25—7.45	7.60	2	7.15	2	—
(3d)	4-MeOC ₆ H ₄	8.12	7.88	7.25—7.50	7.60	2	7.10	2	3.75
(3e)	4-NO ₂ C ₆ H ₄	8.05	7.90	7.28—7.45	7.65	2	7.05	2	—

^a δ (CDCl₃), *J* in Hz.**Table 5.** Preparation of 1-aryl-2-(*N*-arylcarbamoyl)-4,6-diphenylpyridinium tetrafluoroborates

Compd.	⁺ N-Ar	CONHAr'	Time (min)	Yield (%)	M.p. ^a (°C)	Found (%) (Required %)			Molecular formula
						C	H	N	
(4a)	Ph	Ph	80	68	141—143	67.6 (67.7)	4.9 (4.7)	5.3 (5.3)	C ₃₀ H ₂₃ BF ₄ N ₂ O·H ₂ O
(4b)	Ph	4-MeC ₆ H ₄	135	72	245—247	70.4 (70.5)	4.8 (4.8)	5.3 (5.3)	C ₃₁ H ₂₅ BF ₄ N ₂ O
(4c)	4-MeC ₆ H ₄	4-MeC ₆ H ₄	75	65	265—267	73.2 (73.3)	5.0 (5.0)	5.2 (5.2)	C ₃₂ H ₂₇ BF ₄ N ₂ O
(4d)	4-MeC ₆ H ₄	4-ClC ₆ H ₄	135	70	252—254	63.7 (64.0)	4.5 (4.5)	4.8 (4.8)	C ₃₁ H ₂₄ BClF ₄ N ₂ O·H ₂ O
(4e)	4-MeOC ₆ H ₄	4-MeC ₆ H ₄	135	63	257—259	68.6 (68.8)	4.7 (4.8)	5.0 (5.0)	C ₃₂ H ₂₇ BF ₄ N ₂ O ₂
(4f)	4-MeC ₆ H ₄	4-MeOC ₆ H ₄	135	72	248—250	68.5 (68.8)	4.7 (4.8)	— (5.0)	C ₃₂ H ₂₇ BF ₄ N ₂ O ₂
(4g)	4-ClC ₆ H ₄	4-MeC ₆ H ₄	135	60	238—240	63.8 (64.0)	4.6 (4.5)	4.8 (4.8)	C ₃₁ H ₂₄ BClF ₄ N ₂ O·H ₂ O
(4h)	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	75	68	270—272	66.7 (66.9)	4.6 (4.7)	4.9 (4.9)	C ₃₂ H ₂₇ BF ₄ N ₂ O ₃
(4i)	4-MeC ₆ H ₄	4-PhC ₆ H ₄	135	74	185—188	69.8 (69.4)	5.0 (5.1)	— (4.4)	C ₃₇ H ₂₉ BF ₄ N ₂ O·2H ₂ O

^a Obtained as needles, recrystallised from methanol.

obtained by sublimation at 150—180 °C/3.5 mmHg (*ca.* 60%) (Table 7).

^1H N.m.r. Spectra.—All the compounds were characterised spectroscopically. 1-Aryl-2-ethoxycarbonyl-4,6-diphenylpyridinium salts (2a—e) and the corresponding betaines (3a—e) show characteristic ^1H n.m.r. spectra in complete accord with previously described¹⁸ members of these compound classes. The 3-CH and 5-CH signals appear as doublets (*J* 2 Hz) in the region of δ 8.1 and 8.3 respectively; the ethyl ester groups of (2a—e) are seen near δ 4.1 and 1.0 and are absent from the betaines (3a—e) (Tables 2 and 4).

The pyridinium substituted amides (4a—i) show 3-CH and 5-CH doublet resonances at δ 9.0 and 8.7 (*J* 2 Hz) shifted downfield possibly due to the anisotropic effects of the aryl-amido group.

The pyridinium 1-aryl group shows the two protons closest to the electronegative atom shifted downfield at δ 8.3, the remaining protons are observed at *ca.* δ 7.2. The aryl group of the amide function is seen at δ 7.20—7.60, NH as a broad singlet at *ca.* δ 2.5.

Mechanism.—Our results show that nucleophilic substitution of an unactivated aryl nucleus occurs if the system is designed so that the nucleophile is held in close proximity to the carbon which bears the leaving group. In this system aryl displacement occurs *via* a five-membered transition state; previous results^{1,15} in which aryl displacement occurs, using a different system, involved a six-membered cyclic transition

state. Dipolar Meisenheimer spiro complexes have been observed²⁰ as intermediates in aryl migrations. Such complexes have been postulated for Smiles, Chapman, Stevens, and Newman-Kwarts rearrangements²¹ and are likely to be formed in the presently reported reaction.

Synthetic Utility of Present Material.—This synthesis of diarylamines from anilines has synthetic potential as well as mechanistic interest. The overall yields are comparable to those obtained from the Chapman rearrangement from anilines, however activation is not needed and the process does not require the use of high temperatures.

Experimental

^1H N.m.r. spectra were recorded with a Varian EM 360L spectrometer using SiMe₄ as a standard. I.r. spectra were obtained using NaCl plates on a Perkin-Elmer 283B spectrophotometer as solutions in CHBr₃. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

The following were prepared by using literature methods: 2-ethoxycarbonyl-4,6-diphenylpyridinium tetrafluoroborate (m.p. 153—155 °C; lit.,¹⁶ m.p. 154 °C) and trifluoromethanesulphonate (m.p. 182 °C; lit.,¹⁷ m.p. 182—183 °C).

General Method for the Preparation of 1-Aryl-2-ethoxycarbonyl-4,6-diphenylpyridinium Tetrafluoroborates and Trifluoromethanesulphonates (2).—The arylamine (3.3 mmol) was added at 25 °C to a suspension of 2-ethoxycarbonyl-4,6-

Table 6. ¹H N.m.r.^a of 1-aryl-2-(N-arylcarbamoyl)-4,6-diphenylpyridinium tetrafluoroborates

Compd.	N-Ar	CONHAr'	3-CH (1 H, d, J 2)	5-CH (1 H, d, J 2)	4,6-Diphenyl-H (10 H, m)
(4a)	Ph	Ph	9.08	8.75	7.35—7.85
(4b)	Ph	4-MeC ₆ H ₄	8.72	8.55	7.42—7.98
(4c)	4-MeC ₆ H ₄	4-MeC ₆ H ₄	9.05	8.73	7.30—7.83
(4d)	4-MeC ₆ H ₄	4-ClC ₆ H ₄	9.13	8.83	7.33—8.00
(4e)	4-MeOC ₆ H ₄	4-MeC ₆ H ₄	9.00	8.72	7.32—7.80
(4f)	4-MeC ₆ H ₄	4-MeOC ₆ H ₄	9.03	8.76	7.30—7.93
(4g)	4-ClC ₆ H ₄	4-MeC ₆ H ₄	8.95	8.65	7.20—7.80
(4h)	4-MeOC ₆ H ₄	4-MeOC ₆ H ₄	9.02	8.75	7.30—7.91
(4i)	4-MeC ₆ H ₄	4-PhC ₆ H ₄	9.07	8.77	7.50—7.97

Compd.	Ar-H (m)				Ar'-H (m)		NH (1 H, s)	CH ₃ (3 H, s)	CH ₃ O (3 H, s)
	δ	H	δ	H	δ	H			
(4a)	8.30	2	7.20	3	7.20—7.50	5	2.44	—	—
(4b)	8.00	2	7.28	3	7.28—7.60	4	2.45	2.44	—
(4c)	8.30	2	7.20	2	7.20—7.55	4	2.50	2.20, 2.26	—
(4d)	8.43	2	7.26	2	7.16—7.66	4	2.56	2.27	—
(4e)	8.32	2	7.20	2	7.20—7.55	4	2.46	2.25	3.66
(4f)	8.33	2	7.23	2	7.15—7.60	4	2.43	2.13	3.66
(4g)	8.23	2	7.10	2	7.10—7.50	4	2.33	2.10	—
(4h)	8.34	2	7.15	2	7.15—7.60	4	2.42	—	3.63, 3.65
(4i)	8.36	2	7.20	2	7.20—7.46	9	2.43	2.13	—

^a δ[(CD₃)₂SO], J in Hz.

Table 7. Preparation of diarylamines

Compd.	Ar	Ar'	Temp. (°C)	Subln. pressure (mmHg)	Time (h)	Yield (%)	M.p. (°C)	Lit. M.p. (°C)
(8a)	Ph	Ph	150	3	2	65	52—53	53 ^a
(8b)	4-MeC ₆ H ₄	4-MeC ₆ H ₄	180	3	2	65	73—75	78—79 ^b
(8c)	4-MeC ₆ H ₄	4-PhC ₆ H ₄	180	5	4	62	97—98 ^c	—
(8d)	4-MeC ₆ H ₄	4-MeOC ₆ H ₄	150	5	3	55	51—53	55 ^d
(8e)	4-MeC ₆ H ₄	4-ClC ₆ H ₄	180	5	2	58	81—83	85 ^d
(8f)	Ph	4-MeC ₆ H ₄	150	5	2	63	84—86	89 ^e

^a I. Goldberg, *Ber.*, 1907, **40**, 4541. ^b D. G. Daniels, F. T. Naylor, and B. C. Saunders, *J. Chem. Soc., Perkin Trans. 1*, 1951, 3433. ^c *m/z* 259.1361 (*M*⁺. Calc. for C₁₉H₁₇N: *m*, 259.1362). ^d A. R. Sen and A. K. Sen Gupta, *J. Indian Chem. Soc.*, 1957, **34**, 413. ^e F. Ullmann, *Liebigs Ann. Chem.*, 1907, **355**, 312.

Table 8. ¹H N.m.r. spectra^a of diarylamines

Compound	Ar	Ar'	Aromatic protons (m)	4-CH ₃ C ₆ H ₄ (s)	4-CH ₃ OC ₆ H ₄ (3 H, s)	NH (1 H, s)
(8a)	Ph	Ph	6.80—7.30 (10 H)	—	—	5.65
(8b)	4-MeC ₆ H ₄	4-MeC ₆ H ₄	6.85—7.30 (8 H)	2.25 (6 H)	—	5.50
(8c)	4-MeC ₆ H ₄	4-PhC ₆ H ₄	7.00—7.65 (13 H)	2.20 (3 H)	—	5.65
(8d)	4-MeC ₆ H ₄	4-MeOC ₆ H ₄	6.55—7.20 (8 H)	2.20 (3 H)	3.75	5.50
(8e)	4-MeC ₆ H ₄	4-ClC ₆ H ₄	6.95—7.90 (8 H)	2.20 (3 H)	—	5.50
(8f)	Ph	4-MeC ₆ H ₄	6.55—7.30 (9 H)	2.25 (3 H)	—	5.50

^a δ(CDCl₃).

diphenylpyrylium salt (3 mmol) in CH₂Cl₂ (25 ml). The red solution was stirred for the appropriate time (Table 1) at 25 °C. Concentration at 50 °C/25 mmHg and trituration of the residue with Et₂O gave the pyridinium salts which were recrystallised from 95% ethanol (Table 1).

General Method for the Preparation of 1-Aryl-4,6-diphenylpyridinium-2-carboxylates (3).—The 1-aryl-2-ethoxycarbonyl-4,6-diphenylpyridinium salt (10 mmol) was stirred at 25 °C under aqueous NaOH (0.5M; 25 ml, 12.5 mmol) for 24 h. The

white solid was filtered off and washed with water (500 ml) and Et₂O (50 ml) to give the pyridinium-2-carboxylate (Table 3).

General Method for the Preparation of 1-Aryl-2-(N-arylcarbamoyl)-4,6-diphenylpyridinium Tetrafluoroborates (4).—Thionyl chloride (18 mmol) and pyridine (4 mmol) were added to the 1-aryl-4,6-diphenylpyridinium-2-carboxylate (6 mmol) in CH₂Cl₂ (15 ml). The mixture was refluxed for 15 min and the arylamine (18 mmol) added; refluxing was then contin-

ued for the appropriate time (Table 5). The solvent was removed at 50 °C/25 mmHg, and the residue washed successively with water (50 ml) and Et₂O (50 ml). The resulting brown gum was dissolved in methanol (15 ml) and tetrafluoroboric acid (10 mmol) was added to form, after cooling, the 2-(*N*-arylcarbonyl)pyridinium tetrafluoroborate, which was recrystallised from methanol (Table 5).

General Method for the Preparation of Diarylamines (5).

—The 1-aryl-2-(*N*-arylcarbonyl)-4,6-diphenylpyridinium tetrafluoroborate (3 mmol) was dissolved in toluene (30 ml), sodium hydride (99%, 6 mmol) was added and the mixture refluxed for 12 h. The solvent was removed at 60 °C/10 mmHg and the resulting solid washed with water (40 ml) and filtered. Sublimation gave the diarylamine as needles (Table 7). 2,4-Diphenylpicolinic acid was obtained by acidification of the residue (m.p. 150 °C, lit.,²² m.p. 150 °C).

Acknowledgements

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