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N-OXIDES AND RELATED COMPOUNDS—LI[1]

THE SYNTHESIS OF N,N'-LINKED BI(HETEROARYLS)

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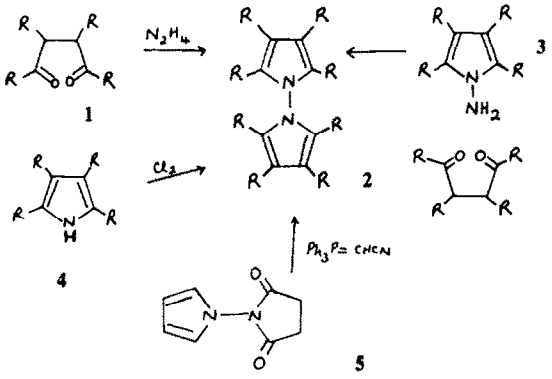
Abstract—Known N,N'-linked biheteroaryls are surveyed. New general synthetic methods are developed and applied for neutral species, for monocations and for dications.

The present study represents the first systematic investigation of synthetic methods for N,N'-linked bi(heteroaryls). Such compounds may be divided into three classes: (i) neutral species, in which an N–N bond links two pyrrole-like nitrogen atoms; (ii) monocations, in which N–N links a pyrrole-like with a pyridine-like N atom; and (iii) dications, in which N–N links two pyridine-like N atoms.

Previous scattered work is mainly concerned with neutral species of type (i), particularly 1,1'-bipyrroyls (**2**) (Scheme 1), which have been synthesised by the reaction

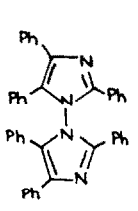


Scheme 1.

of 1,4-diketones (**1**) with hydrazine,[3,4] or with 1-aminopyrroles,[5,6] and by the oxidation of pyrroles (**4**)[7] (a similar reaction is thought to give[8] 9,9'-bicarbazolyls as intermediates), or by Wittig reaction from **5**.[9] The 1,1'-bi(imidazolyl) (**6**) has been obtained by oxidation of 2,4,5-triphenylimidazole,[7] and the 1,1'-bi(quinolonyl) (**7**) by treatment of the corresponding 1-aminoquinolin-4-one with $Pb(OAc)_4$.[10] Finally, 1,1'- (**9**) and 1,2'-bis (benzotriazolyl) (**12**) have been obtained[11] by the routes shown (Scheme 2); the former was quaternised to a monocation.

N,N'-Linked biheteroaryls have considerable potential synthetic utility; we have therefore now developed general procedures for their preparation.

Condensation of N-aminoheteroaryls with 2,5-diethoxytetrahydrofuran. We find that neutral N-amino-heterocycles condense in good yields with 2,5-diethoxytetrahydrofurans to give 1-(N-heteroaryl) pyrroles. This reaction succeeds in the following series: 1-aminopyrrole, 9-aminocarbazole, 1-amino-2-pyridone,



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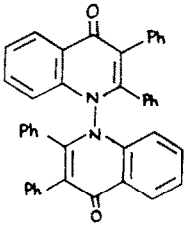

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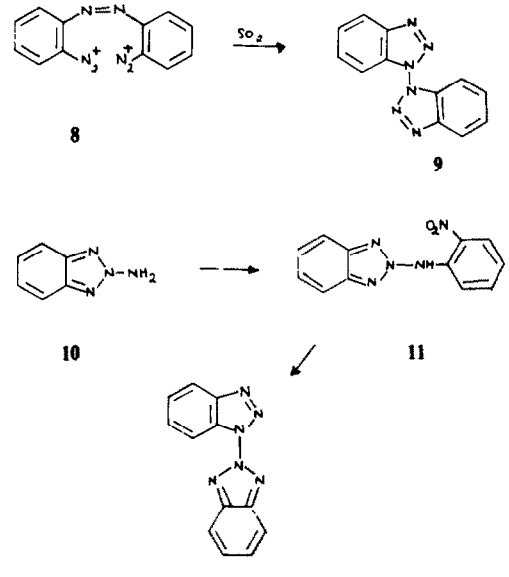
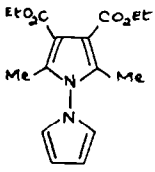
3-amino-4-quinazolone, and 4-amino-1,2,4-triazole. Details are recorded in Table 1 and some of the products illustrated in formulae **13–15**. Compounds were characterised by their NMR spectra (Table 1).

Reaction of 1-aminopyridinium perchlorate with 2,5-diethoxytetrahydrofuran gave only the bis-perchlorate (**16a**), as shown by NMR and analysis; attempts to cyclise **16** failed. Presumably the reduced nucleophilicity of the N–NH_2 group in the cations precludes the ring-closures.

Condensation of 4-amino-1,2,4-triazole with 1,4-diketones and with a 4-pyrone. Two further N,N'-linked triazolyl-pyrroles were prepared from reactions of 4-



Scheme 2.



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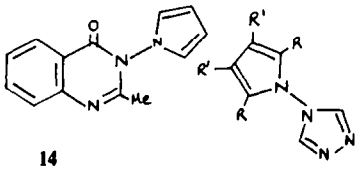

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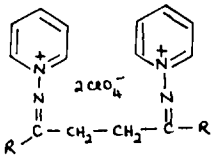
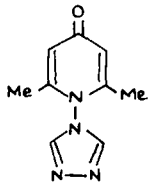
15a R = Me, R' = H
15b R = Me, R' = CO_2Et



16a R = H
16b R = Me

amino-1,2,4-triazole with diketones: the yield (of **15a**) was poor from hexane-2,5-dione, but that of **15b** good from the 3,4-diethoxycarbonyl analogue. The 4-aminotriazole reacted with 2,6-dimethyl-4-pyrone to give the triazolylpyridone (**17**) in poor yield. Reaction of 4-aminotriazole with maleic anhydride gave the acylated product **18**.



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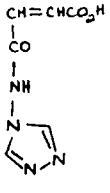

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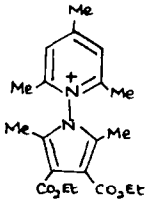
Condensation of N-*aminoheteroaryls with pyrylium cations.* N,N'-linked 1-heteroarylpyridinium cations are formed by reaction of N-aminoheteroaryls with 2,4,6-trimethyl- (Table 2) and 2,4,6-triphenyl-pyrylium cations (Table 3). The yields are generally good and the reaction succeeds in the 1-aminopyrrole (*cf.* **19**), 9-aminocarbazole, 1-aminopyridone (*cf.* **20**), 3-amino-4-quinazolone, 4-aminotriazole (*cf.* **21**) and 1-aminobenzimidazole series.



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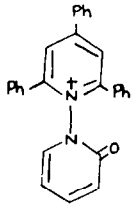

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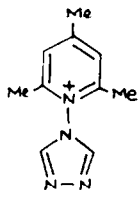

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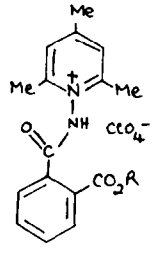
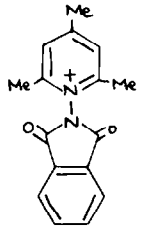


22 R = Me
23 R = Et



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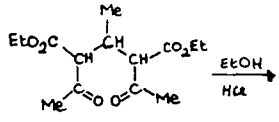
Condensation of N-aminophthalimide with 2,4,6-trimethylpyrylium cation gave **22** or **23** if the reaction were run in methanol or ethanol, respectively, but the ring-closed product **24** in AcOH. Attempted recrystallisation of **24** from hot ethanol gave **23**.

Preparation of an 1-*aminopyridinium compound via a dihydropyridine.* N-Aminophthalimide yields the dihydropyridine **26** by reaction withe keto-ester (**25**). Hydride ion loss to the N-aminopyridinium derivative **27** was effected with triphenylmethyl perchlorate.



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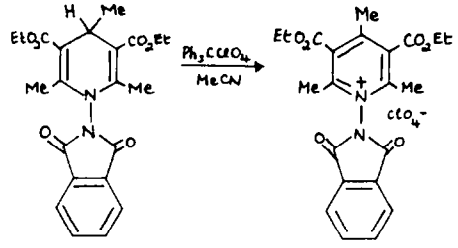

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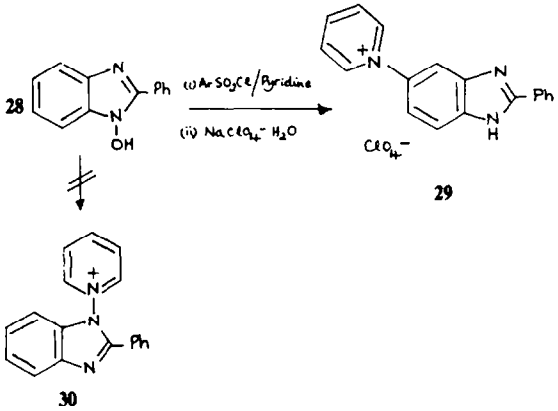
Scheme 3.

Attempted nucleophilic displacement at nitrogen. Attempts to prepare **30** by the reaction **28**→**30** gave instead **29**; nucleophilic attack occurred on carbon instead of nitrogen. This reaction took a similar course with both benzene and mesitylene-sulphonyl chlorides. The product **29** was identified by the IR and NMR spectra. 2,4,5-Triphenylimidazole 1-oxide did not undergo such a reaction.



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Scheme 4.

Reactions with N-*aminopyridinium perchlorate.* Hexane-2,5-dione with N-aminopyridinium perchlorate gave the 1-(1'-pyrrolyl) pyridinium cation **31** together with some of the bisperchlorate (**16b**). Attempts to react N-aminopyridinium perchlorate with 1,4-diphenylbutan-1,4-dione failed as the diketone underwent preferential self-condensation.

Many attempts were made to react 1-aminopyridinium

Table 1. 4-(N-heteroaryl)pyrroles

Starting N-amino compound	M.p. °C	Crystal Form	Solvent for recryst.	Yield %	Found %			Formula	Calc. %			Chemical shift		
					C	H	N		C	H	N	Pyrrole protons		1-Substituent protons
1-Amino-3,4-diethoxycarbonyl-2,5-dimethylpyrrole	58—60	prisms	EtOH-H_2O	72	62.6	6.6	8.9	$C_{16}H_{20}N_2O_4$	63.1	6.6	9.2	3.15	3.5	5.2 (q, 4, J = 7Hz) 7.6 (s, 6) 8.6 (t, 6, J = 7Hz)
9-Amino-carbazole	90—92	needles	EtOH - H_2O	60	81.9	5.4	11.8	$C_{16}H_{12}N_2$	82.7	5.2	12.1			
1-Amino-pyrid-2-one	172—174	needles	EtOH	81	67.2	5.3	16.7	$C_9H_8N_2O$	67.5	5.0	17.5	3.1	3.6	1.5-2.9 (m, 4)
1-Amino-4-methyl-quinol-2-one	157—158	micro crystals	$CHCl_3$	67	74.7	5.3	12.4	$C_{14}H_{12}N_2O$	75.0	5.4	12.5	3.1	3.5	2.8 (s, 1) 1.7-3.6 (m, 4) 7.2 (s, 3)
3-Amino-2-methyl-quinazol-4-one	114—116	micro crystals	EtOH	90	69.6	5.0	18.5	$C_{13}H_{11}N_3O$	69.3	4.9	18.6	3.0	3.4	1.4-2.1 (m, 4) 7.2 (s, 3)
4-Amino-1,2,4-triazole	135—136	needles	EtOH - H_2O	30	53.6	4.7	41.1	$C_6H_6N_4$	53.7	4.5	41.8	2.9	3.5	0.6 (s, 2)

Table 2. 1-(N'-heteroaryl)-2,4,6-trimethyl-pyridinium perchlorates

Parent N-amino compound	Method	M. p. °C	Crystal form	Solvent for recryst.	Yield %	Found % C	Found % H	Found % N	Formula	Calc. % C	Calc. % H	Calc. % N	Chemical shift: Pyridinium protons 2,6 di Me	3,5 di H	4-Me	Chemical shift: Protons of 1-substituent
1-Amino-2,5-dimethylpyrrole	A	ca 170[a]	-		low	-	-	-	$C_{14}H_{19}ClN_2O_4$	53.4	6.1	8.9	7.5	2.2	7.3	3.8 (s, 2) 8.0 (s, 6)
1-Amino-3,4-diethoxycarbonyl-2,5-dimethylpyrrole	A	139—140	needles	H_2O	67	52.1	5.9	6.2	$C_{20}H_{27}ClN_2O_8$	52.3	5.9	6.1	7.5	2.0	7.2	5.3 (q, 4, J = 7Hz) 7.6 (s, 6) 8.4 (t, 6, J = 7Hz)
9-Aminocarbazole	A	169—170[a]	prisms	Me_2CO-Et_2O	90	61.1	5.1	7.1	$C_{20}H_{19}ClN_2O_4$	62.1	4.9	7.2	7.6	2.0	7.2	1.6-3.8 (m, 8)
1-Amino-pyrid-2-one	A	129—130	prisms	Me_2CO	65	49.4	4.9	8.5	$C_{13}H_{15}ClN_2O_5$	49.6	4.8	8.9	7.4	2.1	7.3	1.8-3.1 (m, 4)
	B	126—127		-	86											
1-Amino-quinol-2-one	B	204—206[a]	plates	EtOH	62	55.9	4.7	7.5	$C_{17}H_{17}ClN_2O_5$	56.0	4.7	7.7	7.5	2.0	7.1	1.5-3.5 (m, 6)
4-Amino-1,2,4-triazole	A	200—201[a]	needles	EtOH	90	41.3	4.7	19.1	$C_{10}H_{13}ClN_4O_4$	41.6	4.5	19.4	7.4	2.1	7.2	0.4 (s, 2)
	B	204[a]		-	90											
1-Amino-benzimidazole	B	190—191[a]	needles	EtOH	86	52.8	4.9	12.4	$C_{15}H_{16}ClN_3O_4$	53.3	4.8	12.4	7.4	2.0	7.1	1.5-2.4 (m, 5)
3-Amino-2-methyl-quinazol-4-one	B	174—176[a]	prismatic needles	MeOH	60	53.9	4.7	10.7	$C_{17}H_{18}ClN_3O_5$	53.8	4.8	11.1	7.2	1.9	7.0	1.3-2.0 (m, 4) 7.1 (s, 3)

[a] With decomposition.

Table 3. 1-(N'-heteroaryl)-2,4,-6-triphenyl-pyridinium perchlorates

Parent N-amino compound	Method	M. p. °C	Crystal form	Solvent for recryst.	Yield %	Found %			Formula	Calc. %			Chemical shift	
						C	H	N		C	H	N	Pyridinium 3,5-di H	Other protons
1-Amino-pyrid-2-one	B	236-8[b]	plates	EtOH	78	66.4	4.5	5.4	$C_{28}H_{21}ClN_2O_5$	67.1	4.2	5.6	1.7 (s, 2)	1.9-3.7 (m, 19)
4-Amino-1, 2, 4-triazole	A	274-6[b]	prisms	EtOH	65	62.9	4.2	11.7	$C_{25}H_{19}ClN_4O_4$	63.2	4.0	11.8	1.6 (s, 2)	0.7 (s, 2) 1.7-2.5 (m, 15)
4-Amino-1, 2, 4-triazole[a]	A	195-6[b]	prisms	Me_2CO	85	56.4	4.6	13.2	$C_{20}H_{17}ClN_4O_4$	58.2	4.1	13.6	1.6 (d, 1 J = 1Hz) 1.7 (d, 1 J = 1Hz)	0.5 (s, 2) 1.8-2.5 (m, 10) 7.2 (s, 3)
3-Amino-2-methyl quinazol-4-one	B	210-212[b]	micro crystals	EtOH	68	67.1	4.6	6.9	$C_{32}H_{24}ClN_3O_5$	67.9	4.3	7.4	1.4	1.5-2.5 (m, 19) 7.0 (s, 3)

[a] Condensation with 2-methyl-4, 6-diphenyl pyrylium perchlorate to give 2-methyl-4, 6-diphenyl 1-(1', 2', 4'-triazol'-4'-yl)-pyridinium perchlorate.

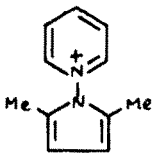
[b] With decomposition.

Table 4. Mono- and di-cation species obtained by methylation of parent N,N-linked biheteroaryls

Parent compound	Method	Solvent for reaction	M.p. °C	Crystal form	Solvent for recryst	Found % C	H	N	Formula	Calc. % C	H	N	Chemical shift Introd. Me	Other signals
1-(1',2',4'-Triazol-4'-yl)-pyrrole	A	CH_2Cl_2	110-112	needles	H_2O	34.0	4.0	21.8	$C_7H_9ClN_4C_4$	33.8	3.6	22.5	5.6 (s, 3)	0.4 (s, 1); 1.1 (s, 1) 2.8 (t, 2, J = 1.5Hz) 3.5 (t, 2, J = 1.5Hz)
3,4-Diethoxycarbonyl-2,5-dimethyl-1-(1',2',4'-triazol-4'-yl)-pyrrole	A	CH_3NO_2	128-130	needles	H_2O	42.3	5.2	13.2	$C_{15}H_{21}ClN_4O_8$	42.8	5.0	13.3	5.6 (s, 3)	-0.3 (s, 1); 0.8 (s, 1) 5.2 (q, 4, J = 7Hz); 7.5 (s, 6) 8.5 (t, 6, J = 7Hz)
2,4,6-Trimethyl-1-(1',2',4'-triazol-4'-yl)-pyridinium perchlorate	A	-	172[b]	plates	MeOH	32.6	4.3	13.7	$C_{11}H_{16}Cl_2N_4O_8$	32.8	4.0	13.9	5.5 (s, 3)	-0.6 (s, 1), 0.4 (s, 1) 2.1 (s, 2); 7.2 (s, 3) 7.3 (s, 6)
2-Methyl-4,6-diphenyl-1-(1',2',4'-triazol-4'-yl)-pyridinium perchlorate	A	-	170-172[b]	micro crystals	Me_2CO-Et_2O	46.5	3.9	4.2	$C_{21}H_{20}Cl_2N_4O_8$	47.8	3.8	10.6	5.7 (s, 3)	-0.4 (s, 1); 0.5 (s, 1) 1.5 (d, 1, J = 4Hz); 1.6 (d, 1, J = 1Hz) 7.0 (s, 3); 1.7-2.4 (m, 10)
2,4,6-Triphenyl-1-(1',2',4'-triazol-4'-yl)-pyridinium perchlorate	A	-	248-250[b]	micro crystals	H_2O	52.4	4.1	9.2	$C_{26}H_{22}Cl_2N_4O_8$	53.0	3.0	9.5	5.9 (s, 3)	-0.3 (s, 1); 0.7 (s, 1) 1.5 (s, 2); 1.7-2.3 (m, 15)
1-(Pyrrol-1'-yl)-pyrid-2-one	B	CH_2Cl_2	136-138	prisms	EtOH	43.6	4.7	10.0	$C_{10}H_{11}ClN_2O_5$	43.7	4.0	10.2	5.6 (s, 3)	1.1-2.4 (m, 4) 2.9 (t, 2, J = 1.5Hz) 3.4 (t, 2, J = 1.5Hz)
2-Methyl-3-(pyrrol-1'-yl)-quinazol-4-one	B	CH_2Cl_2	196-198[b]	plates	MeCN	49.1	4.3	12.5	$C_{14}H_{14}ClN_3O_5$	49.5	4.2	12.4	5.7 (s, 3)	1.4-2.2 (m, 4) 3.1 (t, 2, J = 1.5Hz) 3.5 (t, 2, J = 1.5Hz) 7.2 (s, 3)
2,6-Dimethyl-1-(1',2',4'-triazol-4'-yl)-pyrrol-4-one	n[a]	CH_2Cl_2	224-226[b]	needles	MeCN-Et_2O	31.0	4.0	13.5	$C_{11}H_{16}Cl_2N_4O_9$	31.5	3.8	13.4	5.6 (s, 3) 5.8 (s, 3)	-0.4 (s, 1), 0.6 (s, 1) 2.6 (s, 2) 7.5 (s, 6) (ext. standard)

[a] 0.005 mole was used.

[b] With decomposition.



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cation with pyrylium salts (both 2,4,6-trimethyl and 2,4,6-triphenyl); under acidic or neutral conditions, starting materials were reisolated. Basic conditions (aqueous or anhydrous tertiary amine) gave mixtures of various compounds, but in no case was 1,1'-bipyridinium isolated. Reaction of 1-aminopyridinium with bis(α-chlorobenzal)hydrazine gave 1-benzamidopyridinium involving hydrolysis either before or after reaction.

Quaternary salt formation by N,N'-linked biheteroaryls. Representative neutral N,N'-linked biheteroaryls were converted into monocations, and mono-cationic N,N'-linked biheteroaryls were converted into biscations by methylation with FSO_3Me or MeI/$AgClO_4$. Details are recorded in Table 4. Attempts to O-methylate 1-pyridiniumyl-2-pyridone failed.

EXPERIMENTAL†

N-Amino-heteroaryls. 1 - Amino - 2,5 - dimethylpyrrole,[12] 1 - amino - 3,4 - diethoxycarbonyl - 2,5 - dimethylpyrrole,[13] 9 - amino - carbazole,[14] 1 - amino - 2 - pyridone,[15] 3 - amino - 2 - methyl - 4-quinazolone,[16] 4 - amino - 4H - 1,2,4 - triazole[17] and 1 - amino-pyridinium perchlorate[18] were synthesized by known procedures. 1 - Amino - 2 - quinolone,[15] 1 - amino - 4 - methyl - 2 - quinolone[15] and 1 - amino - benzimidazole[19] were donated by J. Lewis of this laboratory.

Pyrylium perchlorates. 2,4,6 - Trimethylpyrylium perchlorate,[20] 2 - methyl - 4,6 - diphenylpyrylium perchlorate[21] and 2,4,6 - triphenylpyrylium perchlorate[22] were prepared as described.

General procedure for reaction of N - aminoheteroaryls with 2,5 - diethoxytetrahydrofuran. The N-amino compound (0·01 mole), 2,5 - diethoxytetrahydrofuran (1·6 g, 0·01 mole) and AcOH (25 ml) were heated under reflux for 30 min. Solvent was then evaporated at 60°/20 mm. The residue was treated with water and the insoluble product was filtered off, dissolved in hot EtOH decolourised with charcoal and allowed to cool (Table 1).

Application of this procedure to N-aminopyridinium perchlorate gave exclusively *N,N' - bispyridin - 1 - yl - 1,4 - diiminobutane biperchlorate* (1·6 g, 73%) as needles from EtOH m.p. 172–173° dec. (Found: C, 38·2; H, 3·9; N, 12·5. $C_{14}H_{16}Cl_2N_4O_8$ requires: C, 38·3; H, 3·7; N, 12·8%); PMR (60 MHz, CF_3COOH) τ 1·0–2·0 (12) 6·7 (m, 4).

2,5 - Dimethyl - 1 - (1',2',4' - triazol - 4' - yl) - pyrrole. 4 - Amino - 1,2,4 - triazole (3·4 g, 0·04 mole), hexane-2,5-dione (4·6 g, 0·04 mole) and MeOH (50 ml) were heated under reflux for 10 hr. Solvent was evaporated over a water bath and the oily residue was treated with 5% HCl (25 ml). Insoluble solid was filtered off and discarded. After the filtrate was set aside overnight, the crystalline *precipitate* was recrystallized from ethanol as needles (0·4 g, 7%) m.p. 140–142°. (Found: C, 59·1; H, 6·1; N, 34·8. $C_8H_{10}N_4$ requires: C, 59·2; H, 6·2; N, 34·6%); PMR (60 MHz, CF_3COOH) τ 0·6 (s, 2), 4·0 (s, 2), 8·0 (s, 6).

3,4 - Diethoxycarbonyl - 2,5 - dimethyl - 1 - (1',2',4' - triazol - 4' - yl) - pyrrole. 4 - Amino - 1,2,4 - triazole (0·84 g, 0·01 mole), 3,4 - diethoxycarbonylhexane - 2,5 - dione (2·58 g, 0·01 mole) and glacial AcOH (50 ml) were heated under reflux for 2 hr. Solvent was evaporated at 60°/20 mm and the residue was treated with cold water (50 ml). The precipitated *product* (3·3 g) was collected; it recrystallized from EtOH as needles (2·6 g, 85%), m.p. 134–136°. (Found: C, 54·9; H, 5·9; N, 17·7. $C_{14}H_{18}N_4O_4$ requires: C, 54·9; H, 5·9; N, 18·3%); PMR (60 MHz, CF_3COOH) τ 0·4 (s, 2), 5·3 (q, 4, J = 7 Hz), 7·5 (s, 6), 8·4 (t, 6, J = 7 Hz).

2,6 - Dimethyl - 1 - (1',2',4' - triazol - 4' - yl) - pyrid - 4 - one. 4 - Amino - 1,2,4 - triazole (0·84 g, 0·01 mole), 2,6 - dimethyl - 4 - pyrone (1·24 g, 0·01 mole), water (5 ml) and K_2CO_3 (0·25 g) were heated under reflux for 12 hr and cooled overnight. The separated *triazolylpyridone* recrystallized from aqueous EtOH as needles (0·3 g, 16%), m.p. 310°. (Found: C, 56·9; H, 5·4; N, 29·5. $C_9H_{10}N_4O$ requires: C, 56·8; H, 5·3; N, 29·5%); PMR (60 MHz, CF_3COOH) τ 0·4 (s, 2), 2·6 (s, 2), 7·5 (s, 6).

General procedure for the reaction of N-aminoheteroaryls with 2,4,6 - trisubstituted pyrylium perchlorates

(A) The N-aminoheteroaryl (0·01 mole) and the pyrylium perchlorate (0·01 mole) were powdered and added to dry benzene (20–25 ml). The resultant suspension was stirred and heated under reflux for 5 hr. The hot mixture was filtered through a sintered glass funnel. The solid was collected, washed with diethyl ether, dried and recrystallized from EtOH, acetone or water (Tables 2 and 3).

(B) The N-aminoheteroaryl (0·0105 mole) and the pyrylium perchlorate (0·01 mole) were heated under reflux in abs EtOH (25–30 ml) for 6–8 hr. Crystals separated from the cooled mixture and were collected. An additional amount of product could be obtained by dilution of the EtOH filtrate with diethyl ether. (Tables 2 and 3).

1 - (2' - Ethoxycarbonylbenzoylamino) - 2,4,6 - trimethylpyridinium perchlorate. Condensation of N-aminophthalimide with 2,4,6 - trimethylpyrylium perchlorate as in procedure (B) gave prisms (3·1 g; 75%) (from EtOH, dec above 162° without melting). (Found: C, 51·9; H, 5·2; N, 6·9. $C_{18}H_{21}ClN_2O_7$ requires: C, 52·4; H, 5·1; N, 6·8%); PMR (60 MHz, CF_3COOH) τ 1·7–2·2 (m, 4), 2·3 (s, 2), 5·6 (q, 2, J = 7 Hz), 7·0 (s, 6), 7·3 (s, 3), 8·5 (t, 3, J = 7 Hz). N-Aminophthalimide and 2,4,6 - trimethylpyrylium salt in methanol similarly gave *1 - (2' - methoxycarbonylbenzoylamino) - 2,4,6 - trimethylpyridinium perchlorate* (2·5 g, 63%) as prisms (from MeOH) dec above 220°. (Found: C, 51·1; H, 5·0; N, 6·9. $C_{17}H_{19}ClN_2O_7$ requires: C, 51·2; H, 4·8; N, 7·0%), PMR (60 MHz, CF_3COOH) τ 1·9–2·5 (m, 6) 6·1 (s, 3), 7·2 (s, 6), 7·5 (s, 3).

N-Aminophthalimide and 2,4,6-trimethylpyrylium perchlorate in hot glacial acetic acid gave *2,4,6 - trimethyl - 1 - (N' - phthalimido) - pyridinium perchlorate* (1·35 g, 40%) m.p. 162–166° (crude). (Found: C, 50·7; H, 4·3; N, 7·5. $C_{16}H_{15}ClN_2O_6$ requires: C, 52·4; H, 4·1; N, 7·6%); PMR (60 MHz, CF_3COOH) τ 1·9–2·1 (m, 4), 2·3 (s, 2), 7·4 (s, 3), 7·5 (s, 6). *1 - (2',5' - Dimethylpyrrol - 1' - yl)pyridinium perchlorate.* N-Aminopyridinium perchlorate (1·94 g, 0·01 mole), hexane - 2,5 - dione (1·14 g, 0·01 mole), ethanol (50 ml) and H_2SO_4 (0·8 ml) were heated under reflux for 10 hr and cooled overnight at 20°. The *perchlorate* separated; it crystallised from water as long yellow needles (0·5 g, 16%), m.p. 224–226° dec. (Found: C, 48·3; H, 4·8; N, 10·5. $C_{11}H_{13}ClN_2O_4$ requires: C, 48·4; H, 4·8; N, 10·3%); PMR (60 MHz, CF_3COOH) τ 1·0–1·7 (m, 5), 3·9 (s, 2), 7·9 (s, 6). Additional product (0·3 g) can be obtained by slow evaporation of the EtOH filtrate. The reaction mixture contains also a small amount of N,N' - bispyridin - 1 - yl - 2,5 - diimino - hexane biperchlorate as white needles from water m.p. 196–198° dec. (Found: C, 40·7; H, 4·4; N, 12·1. $C_{16}H_{20}Cl_2N_4O_8$ requires: C, 41·1; H, 4·3; N, 12·0%); PMR (60 MHz, CF_3COOH) τ 1–2·0 (m, 10), 6·6–6·8 (m, 4), 7·7–8·0 (m, 6).

3,5 - Diethoxycarbonyl - 1,4 - dihydro - 2,4,6 - trimethyl - 1 - (N' - phthalimido) - pyridine. N-Aminophthalimide (1·62 g) diethyl ethylidenebisacetoacetate (2·86 g), EtOH (5 ml) and 4M-aqueous hydrogen chlorate (6 ml) were kept at 20° for 10 days. The precipitated *dihydropyridine* (1·7 g) crystallised from EtOH as needles m.p. 149–151°C. (Found: C, 63·8; H, 5·8; N, 6·9. $C_{22}H_{24}N_2O_6$ requires: C, 64·0; H, 5·8; N, 6·8%); PMR (CF_3COOH) τ 1·7–2·0 (m, 4), 5·6 (q, 4, J = 7 Hz), 7·8 (s, 6), 8·6 (t, 6, J = 7 Hz), 6·1 (q, 1, J = 8 Hz), 8·7 (d, 3, J = 8 Hz).

3,4 - Diethoxycarbonyl - 2,4,6 - trimethyl - 1 - (N' - phthalimido) - pyridinium perchlorate. The dihydropyridine (0·412 g), triphenylmethyl perchlorate (0·342 g, 0·001 mole) and acetonitrile (5 ml) were left for 12 hr. Diethyl ether was added to complete the precipitation: the *product* crystallised from EtOH as plates, m.p.

†M.ps are uncorrected. They were taken on a Gallenkamp apparatus.

148–150°C (Found: C, 51·2; H, 4·9; N, 5·4; $C_{22}H_{23}ClN_2O_{10}$ requires: C, 51·7; H, 4·5; N, 5·5%); PMR (CF_3COOH) τ 1·7–2·0 (m, 4), 5·3 (q, 4, $J = 7$ Hz), 7·2 (s, 9), 8·5 (t, 6, $J = 7$ Hz).

2 - *Phenyl* - 6(*pyridinium* - 1 - *yl*) - *benzimidazole perchlorate.* 1 - Hydroxy - 2 - phenylbenzimidazole (6·3 g), mesitylene sulphonylchloride (8 g) and pyridine (20·0 g) were heated at 100°C for 1 hr. Excess pyridine was removed at 15 mm/100° and a saturated aqueous solution of sodium perchlorate (100 ml) was added. The mixture was heated to 90°C and insolubles were filtered off and discarded. The filtrate on cooling deposited the *perchlorate* (2·0 g), which after two crystallations from H_2O formed needles (0·5 g), m.p. 208–210°. (Found: C, 57·0; H, 2·0; N, 11·0. $C_{18}H_{14}ClN_3O_4$ requires: C, 58·2; H, 3·8; N, 11·3%).

General procedures for methylation of N,N-linked bi-heteroaryls

(A) The N,N-linked bi-heteroaryl (0·01 mole) was treated with methyl fluorosulphonate (0·02–0·06 mole) at room temp (in solvent or without) for 3–4 days. The product crystallised and was filtered off and washed with dichloromethane or dry diethyl ether. The crude fluorosulphonates were dissolved in the minimum of hot water and poured into 50% aqueous sodium perchlorate soln. Precipitated perchlorate was collected and recrystallised from water or acetone-diethyl ether (Table 4).

(B) The N,N-linked biheteroaryl (0·01 mole), silver perchlorate-acetonitrile complex (3·76 g, 0·01 mole) and 1,2-dichloroethane (20 ml) were stirred at 20°. MeI (7·0 g ~ 0·05 mole) was added dropwise and stirring was continued for 24 hr. The resultant mixture was filtered through sintered glass; solid on the funnel was washed with hot acetonitrile (20 ml) and the combined filtrate was diluted with dry diethyl ether to precipitate the product, which was recrystallized from ethanol or water (Table 4).

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