Preparation of *NN'*-Linked Bi(heteroaryls) from Dehydroacetic Acid and 2,6-Dimethyl-4-pyrone [1]

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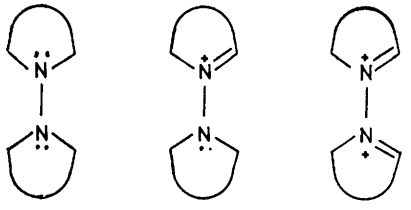
A number of novel *NN'*-linked bi(heteroaryls) (1) and their cations [(2) and (3)] have been prepared by the reaction of dehydroacetic acid (4) or 2,6-dimethyl-4-pyrone (5) with *N*-amino-heterocycles. Analogous reactions of simple hydrazines have also been investigated. In particular, the chemistry of 2,6-dimethyl-1-(1,2,4-triazol-4-yl)-4-pyridone (16) and related cationic species has been investigated in some detail.

ALTHOUGH *NN'*-linked bi(heteroaryls) (1) are potentially useful as synthetic intermediates, only a few compounds belonging to type (1) have been reported. They include *NN'*-bipyrrolyls,[2,3] *NN'*-bi(imidazolyls),[4] 1-(1,2,4-triazol-1-yl)pyrroles,[5] *N*-(1,2,3,4-tetrazol-2-yl)phthalimide,[6] 1,1'- and 1,2'-bi(benzotriazolyls),[7] and *NN'*-bi(quinolonyls).[8] Even less attention has been paid to the preparation of the monocations (2) and the dications (3). Quaternisation of 1,1'-bi(benzotriazolyl) gives a monocation [7] but, apart from this example, the preparation of cationic species of the types (2) and (3) had not been examined until a study of *NN'*-linked bi(heteroaryls) (1) was initiated in this laboratory.[5] Subsequently, the

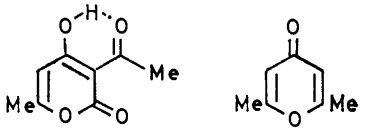


(1) (2) (3)

preparations of a number of new *NN'*-bi(heteroaryls) (1) and cations [(2) and (3)] have been reported.[5,9]

We now report the preparation and chemistry of further examples of *NN'*-bi(heteroaryls) (1) and their cations [(2) and (3)]. In these studies, our efforts to find convenient syntheses of the species (1)—(3) have been centred upon the condensation of *N*-amino-heterocycles with (i) dehydroacetic acid (DHA) (4) and (ii) 2,6-dimethyl-4-pyrone (5).

(i) *Preparation of* NN'*-Linked Bi(heteroaryls) using Dehydroacetic Acid (DHA)* (4).—Recent studies [9] have shown that 1-aminopyridinium salts (6) in hot concentrated hydrochloric acid react with DHA (4), or more



(4) (5)

probably with the 2,6-dimethyl-4-pyrone (5) generated *in situ* by acid-catalysed decarboxylation [(4) ⟶ (5)],[10] giving pyridinio-4-pyridones (7). We have now investigated the reaction of DHA (4) [10] with other *N*-amino-heterocycles, including *N*-aminopyridones (8) and (9). Initial attempts to bring about these condensations in concentrated hydrochloric acid or glacial acetic acid were unsuccessful, apparently owing to the initial formation of an unreactive ammonium salt. However, *N*-aminopyridones (8) and (9) did react with DHA (4) in

[1] *N*-Oxides and Related Compounds, Part 56. Part 55, M. P. Sammes, Ho King Wah, and A. R. Katritzky, *J.C.S. Perkin I*, 1977, 327.

[2] C. Korschun, *Ber.*, 1904, **37**, 2183; C. Bülow and C. Sautermeister, *ibid.*, p. 2697; W. H. Perkin, jun., and S. H. Tucker, *J. Chem. Soc.*, 1921, **119**, 216; C. Chang and R. Adams, *J. Amer. Chem. Soc.*, 1931, **53**, 2353; H. Zimmermann, H. Baumgärtel, and F. Bakke, *Angew. Chem.*, 1961, **73**, 808; K. Schilffarth and H. Zimmermann, *Chem. Ber.*, 1965, **98**, 3124; von W. Flitsch, U. Krämer, and H. Zimmermann, *ibid.*, 1969, **102**, 3268; W. Flitsch and B. Müter, *ibid.*, 1971, 2847; W. Flitsch and H. Peeters, *ibid.*, 1973, **106**, 1731; W. Flitsch and H. Lerner, *Tetrahedron Letters*, 1974, 1677.

[3] N. S. Dokunikhin and G. I. Bystritskii, *Zhur. obshchei. Khim.*, 1963, **33**, 2714.

[4] H. Zimmermann, H. Baumgärtel, and F. Bakke, *Angew. Chem.*, 1961, **73**, 808; T. Hayashi and K. Maeda, *Bull. Chem. Soc. Japan*, 1962, **35**, 2057; H. Baumgärtel and H. Zimmermann, *Z. Naturforsch.*, 1963, **18b**, 406; Yu. A. Rozin, V. E. Blokhin, and Z. V. Pushkareva, U.S.S.R.P. 374,309/1973 (*Chem. Abs.*, 1973, **79**, 53,329*b*).

[5] A. R. Katritzky and J. W. Suwinski, *Tetrahedron Letters*, 1974, 4123; A. R. Katritzky and J. W. Suwinski, *Tetrahedron*, 1975, **31**, 1549.

[6] T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J.C.S. Perkin I*, 1975, 1747.

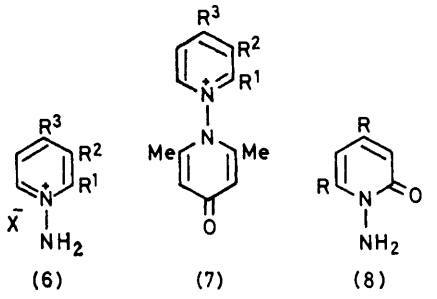
[7] R. J. Harder, R. A. Carboni, and J. E. Castle, *J. Amer. Chem. Soc.*, 1967, **89**, 2643; R. A. Carboni, U.S.P. 3,184,472/1965 (*Chem. Abs.*, 1965, **63**, 4306*b*).

[8] C. W. Rees and M. Yelland, *J.C.S. Perkin I*, 1972, 77.

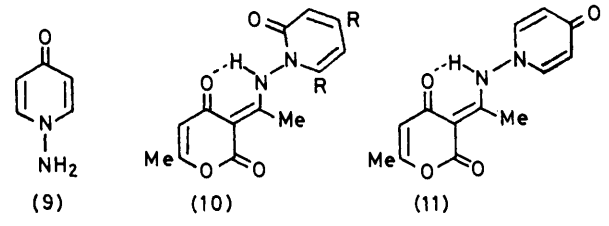
[9] A. R. Katritzky and M. P. Sammes, *J.C.S. Chem. Comm.*, 1975, 247.

[10] R. Gren, *Deut. Apoth.-Ztg.*, 1971, **111**, 219.

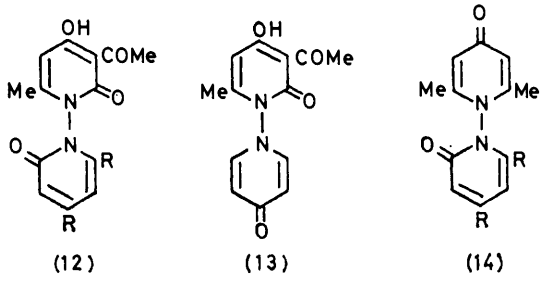
pyridine solution at reflux temperature giving crystalline products which we have formulated as the 2-pyrone derivatives (10) and (11). These structures (10) and (11) are fully supported by elemental analysis and spectral properties but on this basis alone it is not possible to eliminate the alternative 2-pyridone [(12) and (13)]



(6) (7) (8)



(9) (10) (11)



(12) (13) (14)

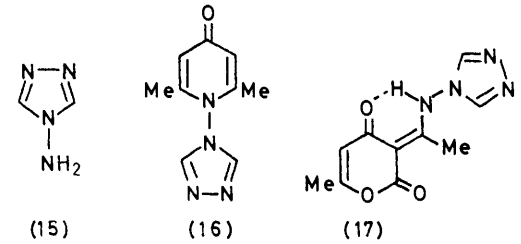
structures. Structures (12) and (13) might reasonably be expected to exhibit i.r. and ^{1}H n.m.r. spectra similar to those of structures (10) and (11). Furthermore, the mass spectral fragmentation patterns are not unambiguous: observed fragment ions could originate by cleavage of a molecular ion corresponding to either the 2-pyrone [(10) and (11)] or 2-pyridone [(12) and (13)] structure. The assignment of structures (10) and (11) is in accord with reported condensation reactions of DHA (4) with amino-derivatives,[11] whereas formation of the isomers (12) and (13) would be unprecedented.

Chemical evidence for the structures (10) and (11) was provided by acid-catalysed decarboxylation of compound (10; R = Ph) which gave the lutidone derivative (14; R = Ph), isolated as its hydrochloride. This product (14; R = Ph) was identical with a sample prepared by an alternative route involving condensation of 2,6-dimethyl-4-pyrone (5) with 1-amino-4,6-diphenyl-2-pyridone (see later).

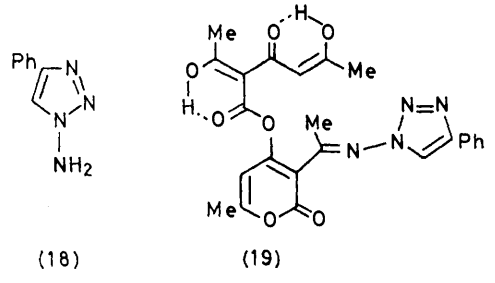
The acid-catalysed rearrangement (10) ⟶ (14) (R = Ph) provides a preparative route to new *NN'*-linked bipyridones but, owing to the rather poor yields and the difficulty encountered in preparing *N*-aminopyridones (8) and (9), this approach was not pursued. This transformation [(10) ⟶ (14)] may involve ring opening followed by cyclisation and decarboxylation. The alternative possibility that acidic hydrolysis gives DHA (4) which is transformed into 2,6-dimethyl-4-pyrone (5) and this intermediate species (5) then condenses with the amino-compound [*e.g.* (8)], giving the observed product (14), must also be considered.

A more useful reaction was that between 4-amino-1,2,4-triazole (15) and DHA (4) in boiling pyridine. In this case 1-(1,2,4-triazol-4-yl)lutidone (16) is formed directly in 65% yield. Presumably the lutidone (16) is formed in a sequence involving initial condensation to give the 2-pyrone (17), which is not isolated but undergoes a reaction involving ready decarboxylation to give the product (16). The reactions of this product (16) are discussed in a later section.

The reaction of DHA (4) with 1-amino-4-phenyl-1,2,3-triazole (18) in pyridine was not as straightforward as the foregoing reaction. An orange, crystalline compound was isolated in moderate yield. Elemental analysis and mass spectra support a constitution $C_{24}H_{22}N_4O_7$, suggesting a condensation reaction between two molecules of DHA (4) and one molecule of the triazole (18). We have assigned the structure (19) to this product and this is supported by the observed spectral properties. The ^{1}H



(15) (16) (17)



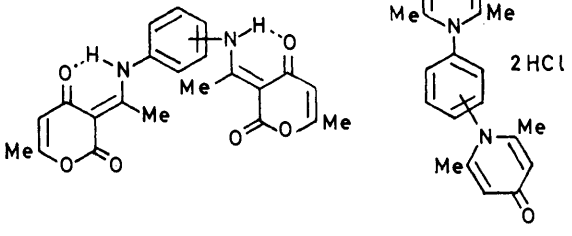
(18) (19)

n.m.r. spectrum shows four distinct methyl groups (τ 7.02, 7.36, 7.86, and 7.92), aromatic protons associated with a phenyl substituent, and three uncoupled hydrogen atoms [H_A (τ 1.72) and H_B and H_C (τ 4.25 and 4.42)].

[11] S. Garratt, *J. Org. Chem.*, 1963, **28**, 1886; D. R. Gupta and R. S. Gupta, *J. Indian Chem. Soc.*, 1965, **42**, 421, 873; S. Iguchi, K. Hisatsune, M. Himeno, and S. Muraoka, *Chem. and Pharm. Bull.* (*Japan*), 1959, **7**, 323; S. Iguchi, A. Inoue, and C. Kurahashi, *ibid.*, 1963, **11**, 385; S. Iguchi and A. Inoue, *ibid.*, 1963, **11**, 390; A. Inoue and S. Iguchi, *ibid.*, 1964, **12**, 381, 382.

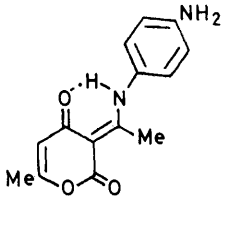
The i.r. spectrum shows absorptions compatible with the carbonyl groups associated with structure (19), and the u.v. absorption bands at 410 and 430 nm are consistent with a conjugated hydrazone structure.

We have also treated DHA (4) with *m*- and *p*-phenylenediamines in pyridine and obtained the anticipated condensation products (20a and b). These compounds in hot hydrochloric acid gave the isomeric bipyridone derivatives (21a and b), isolated and characterised as their hydrochlorides. When the 4-amino-derivative (22) was treated under these conditions, only the bilutidone derivative (21b) was isolated. Evidently (22) is partially hydrolysed to DHA (4); such hydrolyses are thus an



(20) a; *meta*
b; *para*

(21) a; *meta*
b; *para*



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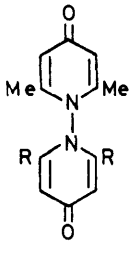

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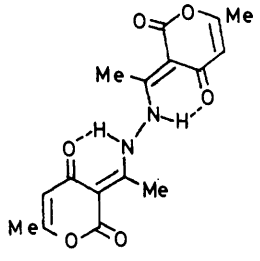


(24)

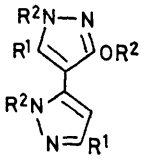
alternative to rearrangements of the type (20) ⟶ (21) under these conditions.

An attractive route to the *NN'*-linked bilutidone (23; R = Me) would be the acid-catalysed rearrangement of the azine (24), which can be prepared by the reaction of two moles of DHA (4) with one mole of hydrazine hydrate. We have found that this reaction [(4) ⟶ (24)] is conveniently executed in pyridine solution at room temperature.

When the azine (24) was heated with aqueous hydrochloric acid for 12 h, the rearranged *NN'*-linked bilutidone (23; R = Me) was indeed isolated, in low yield (3%), as its dihydrochloride, which was fully characterised. This hydrochloride upon treatment with pyridine gave the free *NN'*-linked bi-(4-pyridone) (23; R = Me). Treatment of DHA (4) with two moles of hydrazine hydrate in hot pyridine gave the pyrazole derivative (25; R^1 = Me, R^2 = H) previously encountered by Stollé;[12] this product gives a triacetyl derivative (25; R^1 = Me, R^2 = MeCO) with acetic anhydride.

A similar sequence using dehydrobenzoic acid and hydrazine hydrate gave the analogous pyrazole derivative (25; R^1 = Ph, R^2 = H) and its triacetyl derivative (25; R^1 = Ph, R^2 = MeCO). With benzohydrazide DHA (4) gives the crystalline condensation product (26), which under acidic conditions gave the lutidone derivative (27).

(ii) *Preparation of* NN'-*Linked Bi(heteroaryls) using*



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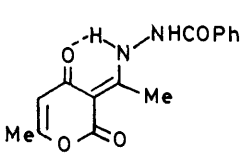

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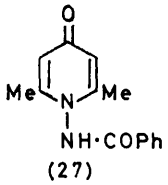
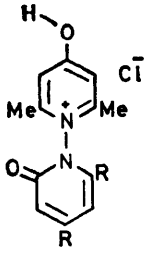


(27)

2,6-*Dimethyl*-4-*pyrone* (5).—Condensation of the *N*-aminopyridones (8) and (9) with 2,6-dimethyl-4-pyrone (5)[13] in hot acid solution gave the *NN'*-linked bipyridones (14; R = H or Ph) and (23; R = H), but yields were rather low. These products are distinct from the products (10) and (11) formed by the similar reactions with dehydroacetic acid (4). These *NN'*-linked bipyridones (14; R = H or Ph) and (23; R = H) were fully characterised by conversion into their hydrochlorides (28; R = H or Ph) and (29), whose structures are assigned on the understanding that 4-pyridones are more basic than 2-pyridones. With 4-amino-1,2,4-triazole (15), the pyrone (5) gave the triazolylpyridone (16),



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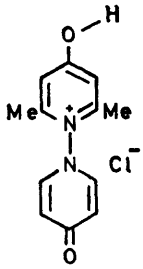

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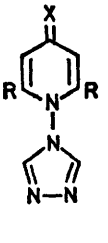


(30)

identical with a sample prepared from dehydroacetic acid (4).

A similar reaction using γ-pyrone and 4-amino-1,2,4-triazole (15) gave the unsubstituted triazolylpyridone (30; R = H, X = O), which with concentrated hydrochloric acid gave its hydrochloride.

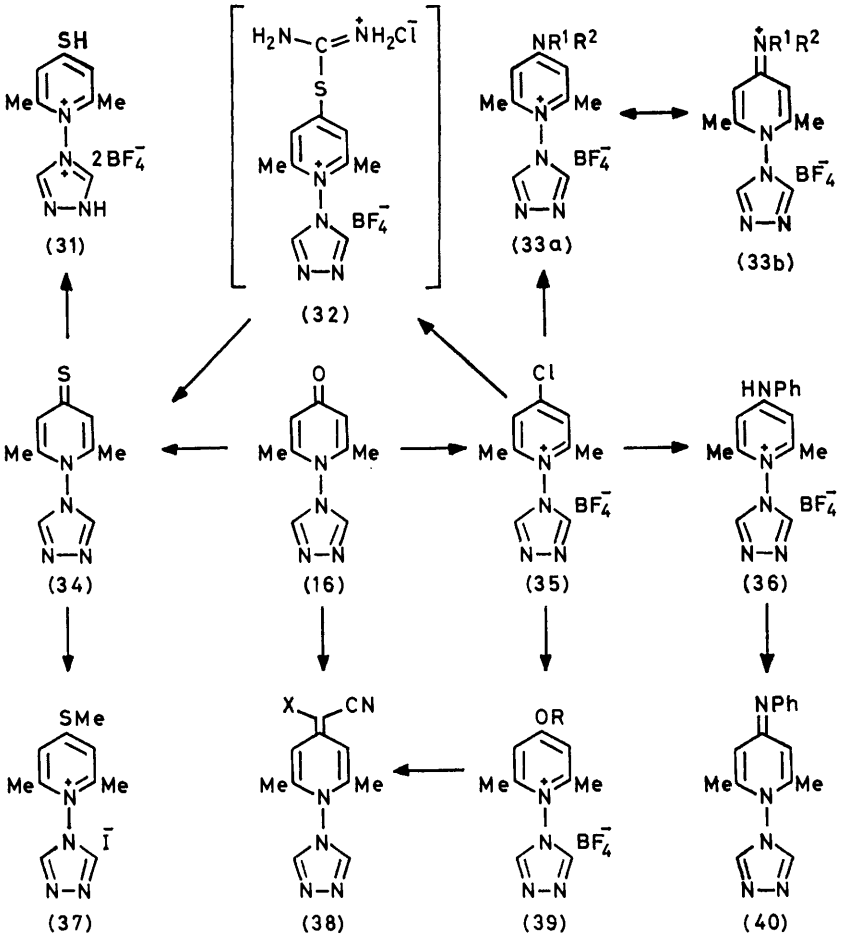
The *NN'*-linked bipyridones (14) and (23) and their cations (28) and (29) were not studied further because of difficulty in preparing them in sufficient quantity. However, the triazolylpyridone (16) is conveniently prepared

[12] R. Stollé, *Ber.*, 1905, **38**, 3023; see also W. H. Perkin, jun., and C. Bernhart, *ibid.*, 1884, **17**, 1522.

[13] M. Ohta and H. Kato, *Bull. Chem. Soc. Japan*, 1959, **32**, 707.

on a moderate scale from dehydroacetic acid (4) (see above) and we have examined its chemistry in some detail.

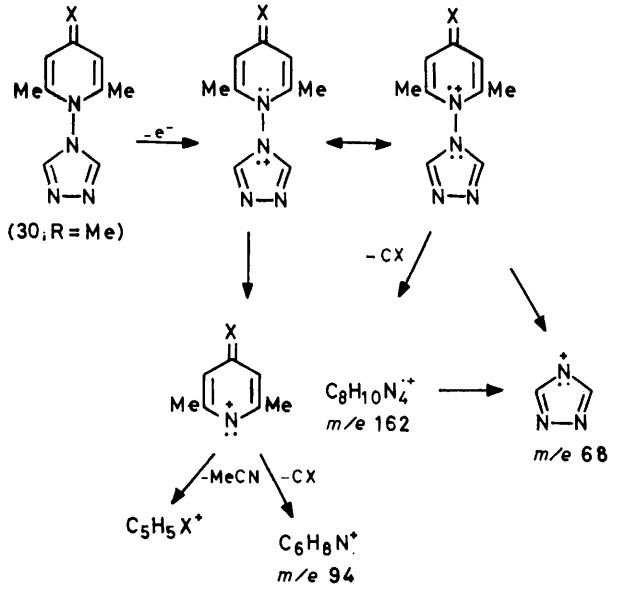
Compound (16) was converted into the yellow, crystalline pyridinethione (34) (Scheme 1) by treatment with phosphorus pentasulphide in hot xylene. This thione (34) with methyl iodide gave the 4-methylthiopyridinium iodide (37) (Scheme 1) and with tetrafluoroboric acid gave the 4-mercaptopyridinium bistetrafluoroborate (31) (Scheme 1). These transformations illustrate the preparation of *NN'*-linked bi(heteroaryls) (1) [*e.g.* (16) and (34)], their monocations (2) [*e.g.* (37)], and their dications (3) [*e.g.* (31)]. Compound (16) is converted in good yield into the 4-chloropyridinium tetrafluoroborate (35) (Scheme 1) by reactions with phosphoryl chloride and treating the resulting, hygroscopic pyridinium chloride with tetrafluoroboric acid. This pyridinium tetrafluoroborate (35) (Scheme 1) is obtained as the hemihydrate and is a convenient intermediate for the preparation of new *NN'*-linked bi(heteroaryls) and their cations. Predictably, the 4-chloro-substituent is easily displaced by nucleophilic reagents. Treatment of the salt (35) with aniline in hot ethanol gave the 4-*N*-phenylamino-pyridinium tetrafluoroborate (36) (Scheme 1), which with alkali gave the imine [(36) ⟶ (40)] (Scheme 1). With secondary amines, an analogous displacement of chloride takes place giving the 4-(tertiary amino)-salts (33). Non-equivalence of the two methyl groups in the ^{1}H n.m.r. spectra of compounds of the general type (33) and (36) indicates that the CN bond at position 4 has some double bond character. Attempts to bring about reaction of the pyridinium salt (35) with sodium borohydride in methanol or methylamine in ethanol resulted in displacement of chloride by alkoxide ion rather than the proposed nucleophile. In this way the 4-alkoxypyridinium tetrafluoroborates (39; R = Me or Et) (Scheme 1) were prepared in 50% yields. The methoxy-derivative (39; R = Me) reacted with malononitrile in hot ethanol giving the 4-dicyanomethylenepyridone (38; X = CN) (Scheme 1), identical with a sample prepared from the pyridone (16) and malononitrile in acetic anhydride [(16) ⟶ (38)] (X = CN) (Scheme 1). Using the latter method, compound (38; X = CO_2Et) was also prepared using ethyl cyanoacetate. Finally the 4-chloropyridinium tetrafluoroborate (35) was converted into the thione (34) by reaction with thiourea in ethanol at reflux



SCHEME 1

temperature. During this transformation an intermediate was observed which was probably the salt (32) (Scheme 1). This compound was not characterised but was decomposed by alkali giving the anticipated thione (34). This indirect route to the thione (34) gives superior yields to those obtained by direct thiation of the pyridone [(16) ⟶ (34)] (Scheme 1).

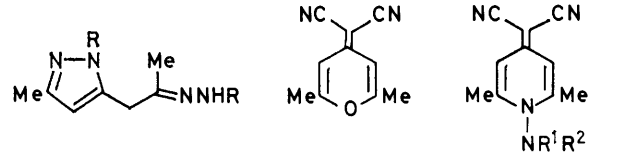
Thus, examples of the *NN'*-linked bi(heteroaryls) of general structure (30; X = O, S, NR, or CR_2) have now



SCHEME 2

been prepared and fully characterised. The structures (16), (34), (38), and (40) (Scheme 1) are fully supported by their spectral properties and their mass spectral fragmentation pattern, which is generalised in Scheme 2.

It has been reported [14] that condensation of 2,6-dimethyl-4-pyrone (5) with hydrazine hydrate gives the *NN'*-linked bipyridone (23; R = Me) which we have prepared as its dihydrochloride, in low yield by an alternative route [(24) ⟶ (23) (R = Me)] (see above).



(41) (42) (43)

We have been unable to repeat the reported preparation of this compound [14] from 2,6-dimethyl-4-pyrone (5) and hydrazine but, by using phenylhydrazine, the pyrazole hydrazone (41; R = Ph) is formed.

When 2,6-dimethyl-4-pyrone (5) is converted into the dicyanomethylene derivative (42) by treatment with malononitrile,[13] formation of pyrazole derivatives [*e.g.* (41)] by condensation with hydrazines is effectively prevented. Thus, we have found that when 4-(dicyanomethylene)-2,6-dimethyl-4*H*-pyran (42) is heated at reflux temperature with ethanolic hydrazine hydrate, the *N*-amino-derivative (43; $R^1 = R^2 = H$) is formed in good yield. This product gives a diacetyl derivative (43; $R^1 = R^2 = MeCO$) with acetic anhydride–pyridine.

We have also found that 2,6-dimethyl-4-pyrone (5) reacts with benzohydrazide in pyridine solution at reflux temperature giving 1-benzamido-2,6-lutidone (27). By this procedure the lutidone (27) was obtained as a hydrate (m.p. 110—112 °C) which could be dehydrated by heating (200—250 °C) under vacuum giving an anhydrous form (m.p. 220 °C). This transformation was easily reversed on exposure to the atmosphere or in ethanol solution. Reaction of this 1-benzamido-2,6-lutidone (27) with malononitrile in acetic anhydride gave the dicyanomethylene derivative (43; R^1 = COPh, R^2 = H).

EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured for Nujol mulls, u.v. spectra for solutions in ethanol, and n.m.r. spectra (60 MHz) for solutions in deuteriochloroform (tetramethylsilane as internal reference). Only significant bands from i.r. spectra are quoted. Mass spectra were determined using a Perkin-Elmer RMU-6E spectrometer. M.p.s were determined using a Kofler hot-stage apparatus. Evaporation refers to the removal of volatile material under diminished pressure. When compounds are stated to be identical, their identity has been established by comparison of m.p. and by mixed m.p., and where appropriate by comparison of i.r. and n.m.r. data and t.l.c. behaviour.

Reactions of Dehydroacetic Acid (4).—(*a*) *With* N-*amino-heterocycles and aromatic amines.* 3-[1-(1,2-*Dihydro*-2-*oxo*-1-*pyridylamino*)*ethylidene*]-6-*methylpyran*-2,4-*dione* (10; R = H). Dehydroacetic acid (4) (0.85 g) [15] and 1-amino-2-pyridone (8; R = H) (0.55 g) [16] in pyridine (20 ml) were heated under reflux (12 h). The solid which separated upon cooling was recrystallised from EtOH to give the *pyran*-2,4-*dione* (10; R = H) (0.58 g, 45%), prisms, m.p. 208—210 °C (Found: C, 59.8; H, 4.7; N, 10.8. $C_{13}H_{12}N_2O_4$ requires C, 60.0; H, 4.7; N, 10.8%); $\lambda_{max.}$ 275 (ε 11 400) and 310 nm (8 000); $\nu_{max.}$ 3 300—3 500 (OH), 1 700, and 1 660 cm^{-1} (C=O); τ (CF_3·CO_2H) 1.2—2.6 (4 H, m, pyridone H), 3.02 (s, CH), 7.00 (s, COMe), and 7.42 (s, CMe); *m/e* 260 ($M^{\cdot+}$).

The following compounds were similarly prepared from 1-amino-4-pyridone (9),[17] 1-amino-4,6-diphenyl-2-pyridone (8; R = Ph),[18] 1-amino-4-phenyl-1,2,3-triazole (18),[19] and *p*-phenylenediamine: 3-[1-(1,4-*dihydro*-4-*oxo*-1-*pyridylamino*)*ethylidene*]-6-*methylpyran*-2,4-*dione* (11) (40%), prisms from EtOH, m.p. 195—197 °C (Found: C, 59.5; H, 4.6; N, 10.9. $C_{13}H_{12}N_2O_4$ requires C, 60.0; H, 4.7; N, 10.8%); $\lambda_{max.}$ 280 nm (ε 15 000); $\nu_{max.}$ 2 500—3 000 (OH), 1 640, and 1 690 cm^{-1} (C=O); τ (CF_3·CO_2H) 1.2 (d, 2 CH, *J* 5 Hz), 2.2 (d, 2 CH, *J* 5 Hz), 3.12 (s, CH), 7.32 (s, COMe), and 7.74

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(s, CMe); *m/e* 260 ($M^{\cdot+}$); 3-[1-(1,2-*dihydro*-2-*oxo*-4,6-*diphenyl*-1-*pyridylamino*)*ethylidene*]-6-*methylpyran*-2,4-*dione* (10; R = Ph) (60%), prisms from EtOH, m.p. 222—224 °C (Found: C, 72.6; H, 5.1; N, 6.9. $C_{25}H_{20}N_2O_4$ requires C, 72.8; H, 4.9; N, 6.8%); $\lambda_{max.}$ 275 (ε 7 500) and 320 nm (13 000); $\nu_{max.}$ 3 100—3 600 (OH), 1 670, and 1 710 cm^{-1} (C=O); τ 2.2—2.8 (10 H, m, aromatic), 3.09 (s, CH), 3.43 (s, CH), 4.30 (s, CH), 7.59 (s, COMe), and 7.88 (s, CMe); *m/e* 412 ($M^{\cdot+}$) and 397, *m** 382 (412 ⟶ 397); 4-[5-*hydroxy*-2-(1-*hydroxyethylidene*)-3-*oxohexanoyloxy*]-6-*methyl*-3-[1-(4-*phenyl*-1,2,3-*triazol*-1-*ylimino*)*ethyl*]*pyran*-2-*one* (19) (40%), orange needles from EtOH, m.p. 246—248 °C (Found: C, 61.0; H, 5.1; N, 11.6. $C_{24}H_{22}N_4O_7$ requires C, 60.3; H, 4.6; N, 11.7%); $\lambda_{max.}$ 275 (ε 4 000), 410 (11 000), and 430 nm (11 500); $\nu_{max.}$ 1 650, 1 700, and 1 730 cm^{-1} (C=O); τ 1.72 (s, CH), 2.0—2.8 (m, aromatic H), 4.25 (s, CH), 4.42 (s, CH), 7.02 (s, Me), 7.36 (s, Me), 7.86 (s, Me), and 7.92 (s, Me); 3-[1-(4-*aminophenylamino*)*ethylidene*]-6-*methylpyran*-2,4-*dione* (22) (80%), prisms from EtOH, m.p. 210—212 °C (Found: C, 64.8; H, 5.4; N, 10.6. $C_{14}H_{14}N_2O_3$ requires C, 65.1; H, 5.5; N, 10.9%); $\lambda_{max.}$ 315 (ε 10 200) and 345 nm (10 200); $\nu_{max.}$ 3 400—3 500 (NH), 1 660, and 1 700 cm^{-1} (C=O); τ 2.7 (d, 2 CH, *J* 8 Hz), 3.0 (d, 2 CH, *J* 8 Hz), 3.93 (s, CH), 5.9br (s, NH_2), 7.08 (s, COMe), and 7.51 (s, CMe); *m/e* 258 ($M^{\cdot+}$); by using two moles of dehydroacetic acid the following compounds were prepared: 6,6′-*dimethyl*-3,3′-p-*phenylenebis*(*iminoethylidyne*)*bis*(*pyran*-2,4-*dione*) (20b) (60%), prisms from $CHCl_3$–EtOH (1 : 1), m.p. >290 °C (Found: C, 64.3; H, 5.1; N, 6.6. $C_{22}H_{20}N_2O_6$ requires C, 64.7; H, 4.9; N, 6.9%); $\lambda_{max.}$ 342 nm (ε 14 500); $\nu_{max.}$ 1 660 and 1 700 cm^{-1} (C=O); τ 2.44 (4 H, s, aromatic), 3.97 (2 H, s, CH), 7.12 (s, COMe), and 7.58 (s, CMe); *m/e* 408 ($M^{\cdot+}$); 6,6′-dimethyl-3,3′-*m*-phenylenebis(iminoethylidyne)-bis(pyran-2,4-dione) (20a) (89%), prisms from EtOH, m.p. 280—282 °C (lit.,[20] 215 °C) (Found: C, 64.4; H, 5.1; N, 6.8. Calc. for $C_{22}H_{20}N_2O_6$: C, 64.7; H, 4.9; N, 6.9%); $\lambda_{max.}$ 220 (ε 7 000) and 265 nm (14 000); $\nu_{max.}$ 1 655 and 1 705 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 2.0—2.7 (4 H, m, aromatic H), 3.40 (2 H, s, CH), 7.14 (6 H, s, CMe), and 7.55 (6 H, s, CMe); *m/e* 408 ($M^{\cdot+}$).

2,6-*Dimethyl*-1-(1,2,4-*triazol*-4-*yl*)-4-*pyridone* (16). Dehydroacetic acid (4) (1.68 g) [15] and 4-amino-1,2,4-triazole (15) (0.84 g) [21] in pyridine (20 ml) were heated under reflux (8 h). After cooling, the solid which separated was recrystallised from EtOH to give the 4-pyridone (16) (1.14 g; 65%), prisms, m.p. 250—290 °C (lit.,[5] 310 °C) (Found: C, 56.9; H, 5.5; N, 29.1. Calc. for $C_9H_{10}N_4O$: C, 56.8; H, 5.3; N, 29.5%); $\lambda_{max.}$ 280 nm (ε 15 400); $\nu_{max.}$ 1 650 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 0.5 (2 H, s, CH), 2.65 (2 H, s, CH), and 7.54 (6 H, s, CMe); *m/e* 190 ($M^{\cdot+}$) and 162, *m** (190 ⟶ 162).

(*b*) *With hydrazines*. 6,6′-*Dimethyl*-3,3′-*hydrazobis*(*iminoethylidyne*)*bis*(*pyran*-2,4-*dione*) (24). Dehydroacetic acid (4) (1.68 g) and hydrazine hydrate (0.25 g) in pyridine (15 ml) were stirred at room temperature (1 h). The solid product was collected and recrystallised from EtOH to give compound (24) (3.0 g, 90%), prisms, m.p. 272—274 °C (lit.,[12] 265 °C) (Found: C, 58.1; H, 4.9; N, 8.2. Calc. for $C_{16}H_{16}N_2O_6$: C, 57.8; H, 4.8; N, 8.4%); $\lambda_{max.}$ 225 (ε 11 400), 310 (9 000), and 390 nm (4 000); $\nu_{max.}$ 1 710 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 3.53 and 3.77 (s, CH), and 7.01, 7.22, 7.58, and 7.64 (s, Me, tautomeric forms).

3-*Hydroxy*-5-*methyl*-4-(3-*methylpyrazol*-5-*yl*)*pyrazole* (25; R^1 = Me, R^2 = H).—Dehydroacetic acid (4) (1.68 g) and hydrazine hydrate (1.0 g) in pyridine (20 ml) were heated under reflux (12 h). Upon cooling, the solid which separated was recrystallised from EtOH to give compound (25; R^1 = Me, R^2 = H) (1.10 g, 60%), prisms, m.p. 250 °C (decomp.) (lit.,[12] 260 °C) (Found: C, 53.6; H, 5.7; N, 31.9. Calc. for $C_8H_{10}N_4O$: C, 53.9; H, 5.6; N, 31.5%); $\lambda_{max.}$ 247 nm (ε 12 000); $\nu_{max.}$ 3 430 (NH) and 1 635 cm^{-1}; τ [$(CD_3)_2SO$] 2.3—3.2br (s, NH or OH), 3.90 (1 H, s, CH), 7.70 (3 H, s, CMe), and 7.80 (3 H, s, CMe); *m/e* 178 ($M^{\cdot+}$). Compound (25; R = H) (0.18 g) was heated under reflux in Ac_2O (5 ml)–HOAc (5 ml) (6 h). The solid product was collected; recrystallisation from EtOH gave the *triacetyl derivative* (25; R^1 = Me, R^2 = MeCO) (0.27 g, 90%) as needles, m.p. 130 °C (Found: C, 55.1; H, 5.5; N, 18.4. $C_{14}H_{16}N_4O_4$ requires C, 55.3; H, 5.3; N, 18.4%); $\lambda_{max.}$ 250 nm (ε 10 100); $\nu_{max.}$ 1 730 and 1 745 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 3.07 (1 H, s, CH), 7.02 (3 H, s, Me), 7.10 (3 H, s, Me), 7.15 (3 H, s, Me), 7.24 (3 H, s, Me), and 7.75 (3 H, s, Me); *m/e* 304 ($M^{\cdot+}$).

In a similar manner by using dehydrobenzoic acid, the following compounds were prepared: 3-*hydroxy*-5-*phenyl*-4-(3-*phenylpyrazol*-5-*yl*)*pyrazole* (25; R^1 = Ph, R^2 = H) (50%), prisms from EtOH, m.p. 271—274 °C (Found: C, 71.4; H, 4.6; N, 18.2. $C_{18}H_{14}N_4O$ requires C, 71.5; H, 4.6; N, 18.5%); $\lambda_{max.}$ 220 (ε 9 000) and 250 nm (13 000); $\nu_{max.}$ 3 400 (NH) and 1 635 cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 2.5—4.0 (m, aromatic H); *m/e* 302 ($M^{\cdot+}$); and its *triacetyl derivative* (25; R^1 = Ph, R^2 = COMe) (50%), prisms from EtOH, m.p. 188—190 °C (Found: C, 67.0; H, 4.7; N, 13.1. $C_{24}H_{20}N_4O_4$ requires C, 67.3; H, 4.7; N, 13.1%); $\lambda_{max.}$ 220 (ε 8 000) and 268 nm (9 800); $\nu_{max.}$ 1 740—1 775 cm^{-1} (C=O); τ 1.8—3.5 (11 H, m, aromatic H) and 7.2—7.8 (3 H, singlets—diastereoisomers); *m/e* 428 ($M^{\cdot+}$), 385, 342, and 299, *m** (428 ⟶ 385), *m** (385 ⟶ 342), *m** (342 ⟶ 299).

3-[1-(2-*Benzoylhydrazino*)*ethylidene*]-6-*methylpyran*-2,4-*dione* (26). Dehydroacetic acid (4) (1.68 g) and benzohydrazide (1.36 g) in pyridine solution (20 ml) were heated under reflux (2 h). The crystalline product was collected; recrystallisation from EtOH gave *compound* (26) (1.7 g, 60%), prisms, m.p. 213—216 °C (Found: C, 63.0; H, 4.7; N, 10.1. $C_{15}H_{14}N_2O_4$ requires C, 62.9; H, 4.9; N, 9.8%); $\lambda_{max.}$ 235 (ε 10 600) and 330 nm (9 200); $\nu_{max.}$ 1 655, 1 675, and 1 700 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 1.8—2.7 (5 H, m, Ph), 3.45 (1 H, s, CH), 6.98 (3 H, s, CMe), and 7.60 (3 H, s, CMe); *m/e* 286 ($M^{\cdot+}$).

Acid-catalysed Decarboxylations.—Compound (10; R = Ph) (0.41 g) in 50% aqueous HCl (20 ml) was heated under reflux (12 h). Evaporation and recrystallisation of the residue from EtOH gave 1-(1,2-*dihydro*-2-*oxo*-4,6-*diphenyl*-1-*pyridyl*)-4-*hydroxy*-2,6-*dimethylpyridinium chloride* (28; R = Ph) (0.16 g, 40%), m.p. 247 °C, identical with a sample prepared from 2,6-dimethyl-4-pyrone (5) (see later).

The following compounds were prepared by similar transformations. Compound (20b) gave 4,4′-*dihydroxy*-2,2′,6,6′-*tetramethyl*-1,1′-p-*phenylenedipyridinium dichloride* (21b) (40%), crystallised from EtOH as the hydrate, prisms, m.p. 254—257 °C (decomp.) (Found: C, 58.1; H, 5.7; N, 7.1. $C_{20}H_{22}Cl_2N_2O_2,H_2O$ requires C, 58.4; H, 5.8; N, 6.8%); $\lambda_{max.}$ 215 (ε 4 600) and 268 nm (7 200); $\nu_{max.}$ 1 635 cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 2.09 (4 H, s, CH), 2.68 (4 H, s, CH), and 7.56

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(12 H, s, CMe); *m/e* 320 ($M^{\cdot+}$ − $H_3O^+Cl^-$); compound (20a) gave 4,4′-*dihydroxy*-2,2′,6,6′-*tetramethyl*-1,1′-m-*phenylenedipyridinium dichloride* (21a) (38%), recrystallised from EtOH as the hydrate, prisms, m.p. 282 °C (Found: C, 58.2; H, 5.7; N, 6.8. $C_{20}H_{22}Cl_2N_2O_2,H_2O$ requires C, 58.4; H, 5.8; N, 6.8%); $\lambda_{max.}$ 215 (ε 7 000) and 268 nm (12 000); $\nu_{max.}$ 1 635 cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 1.6—2.3 (4 H, m, aromatic H), 2.66 (4 H, s, CH), and 7.57 (12 H, s, CMe); *m/e* 320 ($M^{\cdot+}$ − $H_3O^+Cl^-$); the azine (24) gave 2,2′,6,6′-*tetramethyl*-1,1′-*bi*-4-*pyridone* (23; R = Me) *dihydrochloride* (3%), crystallised from EtOH–Et_2O, prisms, m.p. 315 °C (Found: C, 52.8; H, 5.6; N, 8.7. $C_{14}H_{18}Cl_2N_2O_2$ requires C, 53.0; H, 5.7; N, 8.8%); $\lambda_{max.}$ 232 (ε 7 200) and 275 nm (11 200); $\nu_{max.}$ 1 620 cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 2.25br (4 H, s, CH) and 7.45 (12 H, s, Me): compound (26) gave 1-*benzamido*-2,6-*lutidone* (27) (33%) identical with a sample prepared from 2,6-dimethyl-4-pyrone (5) and benzohydrazide (see later).

N,N′-*Bi*-(2,6-*lutidone*) (23; R = Me).—The dihydrochloride of (23; R = Me) (0.5 g) and aqueous pyridine (50%) (10 ml) upon mixing at room temperature underwent an exothermic reaction. After stirring (20 min), $CHCl_3$ (25 ml), EtOH (25 ml), and H_2O (20 ml) were added. The $CHCl_3$ extract was evaporated and the residue was recrystallised from EtOH giving *compound* (23; R = Me) as a hemihydrate (0.1 g, 25%), prisms, m.p. 313—316 °C (Found: C, 66.3; H, 6.4; N, 10.9. $C_{14}H_{16}N_2O_2,0.5H_2O$ requires C, 66.4; H, 6.7; N, 11.1%); $\lambda_{max.}$ 220 (ε 5 200) and 275 nm (13 000); $\nu_{max.}$ 1 650 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 2.25 (4 H, s, CH) and 7.35 (12 H, s, Me).

Reactions of 2,6-*Dimethyl*-4-*pyrone* (5).—(a) *With* N-*amino-heterocycles*. 2,6-Dimethyl-4-pyrone (5) (0.25 g) [13] and 1-amino-2-pyridone (8; R = H) (0.22 g) [16] in glacial acetic acid (10 ml) were heated under reflux (50 h). Evaporation and recrystallisation of the residue from EtOH gave 2′,6′-*dimethyl*-1,1′-*bipyridine*-2,4′-*dione* (14; R = H) (70 mg, 15%), prisms, m.p. 207—209 °C; $\lambda_{max.}$ 275 nm (ε 14 000); τ ($CF_3{\cdot}CO_2H$) 1.4—1.9 (2 H, m), 2.4—2.8 (4 H, m), and 7.53 (6 H, s, CMe); *m/e* 216 ($M^{\cdot+}$). Treatment of compound (14; R = H) with conc. HCl in EtOH at reflux temperature (5 h) gave, upon cooling, the *hydrochloride* (28; R = H) (70%), prisms from EtOH, m.p. 259—261 °C (Found: C, 56.6; H, 5.2; Cl, 13.9; N, 10.8. $C_{12}H_{13}ClN_2O_2$ requires C, 57.0; H, 5.2; Cl, 14.0; N, 11.1%); $\lambda_{max.}$ 275 (ε 12 000) and 300 nm (8 000); $\nu_{max.}$ 1 675 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 1.8—3.3 (6 H, m, aromatic) and 7.52 (6 H, s, Me); *m/e* 217 ($M^{\cdot+}$ − ^{35}Cl).

Alternatively, 2,6-dimethyl-4-pyrone (5) (0.25 g) and 1-amino-2-pyridone (0.22 g) in conc. HCl (10 ml) at reflux temperature (24 h) gave the hydrochloride (28; R = H), m.p. 259—261 °C, identical with the sample described above.

In a similar sequence the following two compounds were prepared: 2,6-*dimethyl*-1,1′-*bi*-4-*pyridone* (23; R = H) (18%), prisms from EtOH, m.p. 210—212 °C (Found: N, 12.9. $C_{12}H_{12}N_2O_2$ requires N, 13.0%); $\lambda_{max.}$ 280 nm (ε 15 200); $\nu_{max.}$ 1 650 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 1.3br (d, CH), 2.3br (d, CH), and 2.75br (s, CH); *m/e* 216 ($M^{\cdot+}$); and the *hydrochloride* (29) (85%), hydrated prisms from EtOH, m.p. 245—247 °C (Found: C, 53.0; H, 5.0; N, 10.1. $C_{12}H_{13}ClN_2O_2,H_2O$ requires C, 53.2; H, 5.6; N, 10.4%); $\lambda_{max.}$ 275 nm (ε 9 000); τ ($CF_3{\cdot}CO_2H$) 1.4 (d, CH, *J* 7 Hz), 2.4 (d, CH, *J* 7 Hz), and 7.18 (6 H, s, Me); *m/e* 217 ($M^{\cdot+}$ − ^{35}Cl).

2′,6′-*Dimethyl*-4,6-*diphenyl*-1,1′-*bipyridine*-2,4′-*dione hydrochloride* (28; R = Ph). 2,6-Dimethyl-4-pyrone (5) (1.24 g) [13] and 1-amino-4,6-diphenyl-2-pyridone (8; R = Ph) (2.62 g) [18] in conc. HCl (20 ml) were heated under reflux. Evaporation and recrystallisation of the residue from EtOH gave the *hydrochloride* (28; R = Ph) (2.0 g, 50%) as prisms, m.p. 246—248 °C (Found: C, 71.2; H, 5.0; N, 6.8. $C_{24}H_{21}ClN_2O_2$ requires C, 71.2; H, 5.2; N, 6.9%); $\lambda_{max.}$ 280 (ε 14 000) and 330 nm (5 600); $\nu_{max.}$ 1 680 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 2.1—2.9 (14 H, m, aromatic) and 7.43 (6 H, s, Me); *m/e* 369 ($M^{\cdot+}$ − ^{35}Cl).

2,6-*Dimethyl*-1-(1,2,4-*triazol*-4-*yl*)-4-*pyridone* (16). 2,6-Dimethyl-4-pyrone (5) (1.24 g) and 4-amino-1,2,4-triazole (15) (0.84 g) [21] in glacial acetic acid (20 ml) at reflux temperature (12 h) gave, after evaporation and recrystallisation from EtOH, the pyridone (16) (0.76 g, 40%), m.p. 247—290 °C (decomp.), identical with specimen prepared as described above.

In a similar manner using pyridine as solvent the following compounds were prepared: 1-(1,2,4-*triazol*-4-*yl*)-4-*pyridone* (30; R = H, X = O) (30%) as prisms (from pyridine), m.p. 210 °C; $\lambda_{max.}$ 210 (ε 2 800) and 265 nm (11 000); $\nu_{max.}$ 1 650 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 0.30 (2 H, s, CH), 1.10 (2 H, d, CH, *J* 5 Hz), and 2.35 (2 H, d, CH, *J* 5 Hz); *m/e* 162 ($M^{\cdot+}$). Treatment of this product with conc. HCl (1 ml) in warm EtOH (10 ml) gave the *hydrochloride* (80%), prisms, m.p. 200 °C (decomp.) (Found: C, 42.6; H, 3.7; Cl, 17.8; N, 28.3. $C_7H_7ClN_4O$ requires C, 42.3; H, 3.5; Cl, 17.9; N, 28.2%); $\lambda_{max.}$ 265 nm (ε 13 800); $\nu_{max.}$ 1 640 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 0.0—3.0br (CH); *m/e* 163 ($M^{\cdot+}$ − ^{35}Cl) and 162 ($M^{\cdot+}$ − HCl).

(b) *With hydrazines*. (i) *Benzohydrazide*. 2,6-Dimethyl-4-pyrone (5) (1.24 g) and benzohydrazide (1.36 g) in pyridine (20 ml) were heated under reflux (24 h). After cooling, the solid which separated was recrystallised from EtOH giving 1-*benzamido*-2,6-*lutidone* (27) as hydrated prisms (1.56 g, 60%), m.p. 110—112 °C (Found: C, 64.2; H, 6.1; N, 10.7. $C_{14}H_{14}N_2O_2,H_2O$ requires C, 64.6; H, 6.2; N, 10.8%); $\lambda_{max.}$ 280 nm (ε 5 000); $\nu_{max.}$ 3 000—3 500 (NH and OH) and 1 670 cm^{-1} (C=O); τ [$(CD_3)_2SO$] 1.7—2.5 (5 H, m, Ph), 3.75 (2 H, s, CH), 4.5—5.5br (NH), and 7.69 (6 H, s, Me). When a sample of compound (27) was heated at 200—250 °C *in vacuo* (1 h) an anhydrous form was obtained, m.p. 220 °C (Found: C, 68.9; H, 5.9; N, 11.8. $C_{14}H_{14}N_2O_2$ requires C, 69.4; H, 5.8; N, 11.5%).

(ii) *Phenylhydrazine*. 2,6-Dimethyl-4-pyrone (5) (1.24 g) and phenylhydrazine (2.2 g) in pyridine (10 ml) were heated at reflux temperature. Evaporation gave a gum which was washed with water (3 × 10 ml), and the residue was then dissolved in ether (15 ml). Ice-cold water (20 ml) was added to the ethereal solution and scratching gave a precipitate which was collected and washed with ice–water. The colourless product, which is stable under vacuum but which decomposes in the atmosphere, was identified as 5-*acetonyl*-3-*methyl*-1-*phenylpyrazole phenylhydrazone* (41; R = Ph) (0.6 g, 20%), prisms, m.p. 80—82 °C (Found: N, 18.1; H, 6.6. $C_{19}H_{20}N_4$ requires N, 18.5; H, 6.3%); $\lambda_{max.}$ 270 nm (ε 13 000); $\nu_{max.}$ 3 300(NH) and 1 600 cm^{-1} (C=N, C=C); τ 2.4—2.8 (10 H, m, Ph), 3.85 (1 H, s, CH), 6.25 (2 H, s, CH_2), and 7.7 and 7.8 (6 H, s, Me).

Reaction of 1-*Benzamido*-2,6-*lutidone* (27) *with Malononitrile*.—Compound (27) (2.42 g) and malononitrile (0.66 g) were treated with boiling Ac_2O (15 ml) (8 h). Evaporation and recrystallisation from aqueous EtOH gave 1-*benzamido*-4-*dicyanomethylene*-1,4-*dihydro*-2,6-*dimethylpyridine* (43; R^1 = COPh, R^2 = H) (25%), prisms, m.p. 277—280 °C (Found: C, 70.1; H, 4.6; N, 19.4. $C_{17}H_{14}N_4O$ requires

C, 70.3; H, 4.8; N, 19.3%); $\lambda_{max.}$ 355 nm (ε 8 500); $\nu_{max.}$ 2 180 (C≡N) and 1 700 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 1.7—2.1 (5 H, m, Ph), 2.70 (2 H, s, CH), and 7.20 (6 H, s, Me).

Reaction of 4-*Dicyanomethylene*-4H-2,6-*dimethylpyran* (42) [13] *with Hydrazine Hydrate*.—Compound (42) (1.7 g) and hydrazine hydrate (1.5 g) in EtOH (20 ml) were heated under reflux (3 h). After cooling, the solid product was collected and recrystallisation from EtOH gave 1-*amino*-4-*dicyanomethylene*-1,4-*dihydro*-2,6-*dimethylpyridine* (43; $R^1 = R^2 = H$) (1.1 g, 60%), prisms, m.p. 240 °C (decomp.) (Found: C, 64.2; H, 5.4; N, 30.3. $C_{10}H_{10}N_4$ requires C, 64.5; H, 5.6; N, 30.1%); $\lambda_{max.}$ 212 (ε 4 000), 242 (3 000), and 350 nm (13 000); $\nu_{max.}$ 3 300 (NH), 2 170 (C≡N), and 1 640 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 2.40br (2 H, s, CH) and 7.15 (6 H, s, Me). This product (1.86 g) and Ac_2O (5 ml) in pyridine (10 ml) were heated under reflux (5 h). The solid product was collected; recrystallisation from EtOH gave 1-*diacetylamino*-4-*dicyanomethylene*-1,4-*dihydro*-2,6-*dimethylpyridine* (43; $R^1 = R^2 =$ MeCO) (1.3 g, 50%), prisms, m.p. 230—232 °C (Found: C, 61.8; H, 5.1; N, 20.7. $C_{14}H_{14}N_4O_2$ requires C, 62.2; H, 5.2; N, 20.7%); $\lambda_{max.}$ 245 (ε 4 000) and 360 nm (15 000); $\nu_{max.}$ 2 200 (C≡N) and 1 760 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 2.95 (2 H, s, CH), 7.45 (6 H, s, Me), and 7.65 (6 H, s, Me); *m/e* 270 ($M^{\cdot+}$), 228, and 186.

Reactions of 2,6-*Dimethyl*-1-(1,2,4-*triazol*-4-*yl*)-4-*pyridone* (16).—(a) *With phosphorus pentasulphide*. Compound (16) (1.9 g) and P_4S_{10} (4.4 g) in xylene (50 ml) were heated under reflux (8 h). Evaporation of the filtrate and recrystallisation from EtOH–Et_2O gave 2,6-*dimethyl*-1-(1,2,4-*triazol*-4-*yl*)*pyridine*-4-*thione* (34) (0.3 g, 15%), yellow prisms, m.p. 165—167 °C (Found: S, 16.0. $C_9H_{10}N_4S$ requires S, 15.5%); $\lambda_{max.}$ 275 nm (ε 13 000); $\nu_{max.}$ 1 050 cm^{-1} (C=S); τ ($CF_3{\cdot}CO_2H$) 0.50 (s, CH), 2.15 (s, CH), and 7.50 (s, Me); *m/e* 206 ($M^{\cdot+}$).

(b) *With malononitrile*. Compound (16) (1.9 g) and malononitrile (0.66 g) in Ac_2O (10 ml) were heated under reflux (2 h). The solid which separated upon cooling was recrystallised from glacial acetic acid to give 4-*dicyanomethylene*-2,6-*dimethyl*-1-(1,2,4-*triazol*-4-*yl*)-4-*pyridone* (38; X = CN) (1.7 g, 70%), prisms, m.p. 278—280 °C (Found: C, 60.6; H, 4.5; N, 34.9. $C_{12}H_{10}N_6$ requires C, 60.5; H, 4.2; N, 35.3%); $\lambda_{max.}$ 360 nm (ε 14 000); $\nu_{max.}$ 2 200 cm^{-1} (C≡N); τ [$(CD_3)_2SO$] 0.75 (s, CH), 3.00 (s, CH), and 7.80 (s, Me); *m/e* 238 ($M^{\cdot+}$), 170, and 155, *m** 121 (238 ⟶ 170), *m** 142 (170 ⟶ 155).

(c) *With ethyl cyanoacetate*. Compound (16) (0.19 g) and ethyl cyanoacetate (0.11 g) in Ac_2O (10 ml) were heated under reflux (8 h). Upon cooling a solid separated which was recrystallised from EtOH to give 2,6-*dimethyl*-1-(1,2,4-*triazol*-4-*yl*)-4-*pyridone* (38; X = CO_2Et) (0.17 g, 60%), prisms, m.p. 223—225 °C (decomp.) (Found: C, 55.1; H, 5.4; N, 22.7. $C_{14}H_{15}N_5O_2,H_2O$ requires C, 55.4; H, 5.6; N, 23.1%); $\lambda_{max.}$ 370 nm (ε 13 000); $\nu_{max.}$ 1 670 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$) 0.5 (s, CH), 0.6 (s, CH), 5.71 (q, CH_2, *J* 7 Hz), 7.84 (s, CMe), and 8.67 (t, $CH_2{\cdot}CH_3$, *J* 7 Hz); *m/e* 285 ($M^{\cdot+}$).

(d) *With phosphoryl chloride*. Compound (16) (1.9 g) was stirred (10 h) with $POCl_3$ (10 ml). The solid product was washed with dry ether (3 × 20 ml) and dried *in vacuo* (24 h). The product, 4-chloro-2,6-dimethyl-1-(1,2,4-triazol-4-yl)-pyridinium chloride, m.p. 203—205 °C, is hygroscopic and was kept under dry ether and used without further purification. It was fully characterised by conversion into the tetrafluoroborate (35). Thus, the crude chloride (2.5 g) in HBF_4 (5 ml) was stirred (4 h). The solid product was washed with ether (3 × 20 ml) and identified as the hemihydrate of 4-*chloro*-2,6-*dimethyl*-1-(1,2,4-*triazol*-4-*yl*)*pyridinium tetrafluoroborate* (35) (2.2 g, 75%), prisms, m.p. 215—217 °C (Found: C, 35.4; H, 3.6; N, 17.9. $C_9H_{10}BClF_4N_4,0.5H_2O$ requires C, 35.4; H, 3.6; N, 18.3%); $\lambda_{max.}$ 280 nm (ε 15 000); $\nu_{max.}$ 1 050br cm^{-1} (BF_4^-); τ ($CF_3{\cdot}CO_2H$) 0.5 (s, CH), 1.90 (s, CH), and 7.28 (s, CMe).

Reactions of 2,6-*Dimethyl*-1-(1,2,4-*triazol*-4-*yl*)*pyridine*-4-*thione* (34).—(a) *With tetrafluoroboric acid*. Compound (34) (0.62 g) and HBF_4 (5 ml) in EtOH (15 ml) were stirred at room temperature (20 min) and then gently heated until the thione had dissolved. Upon cooling a solid separated which was recrystallised from EtOH and identified as 4-*mercapto*-2,6-*dimethyl*-1-(1,2,4-*triazol*-1-*io*)*pyridinium bistetrafluoroborate* (31) (0.78 g, 70%), prisms, m.p. 96—98 °C (Found: C, 28.1; H, 3.2; N, 14.7. $C_9H_{12}B_2F_8N_4S$ requires C, 28.3; H, 3.1; N, 14.7%); $\lambda_{max.}$ 215 (ε 5 000) and 260 nm (9 000); $\nu_{max.}$ 2 560sh and 1 050 cm^{-1} (BF_4^-); τ ($CF_3{\cdot}CO_2H$) 0.10 (s, CH) 2.50 (s, CH), and 7.40 (s, CMe); *m/e* 206 ($M^{\cdot+}$ − HBF_4).

(b) *With methyl iodide*. Compound (34) (0.5 g) in EtOH (15 ml) was heated under reflux (24 h) with MeI (5 ml). The solid product was washed with hot EtOH and identified as 2,6-*dimethyl*-4-*methylthio*-1-(1,2,4-*triazol*-4-*yl*)*pyridinium iodide* (37) (0.6 g, 80%), prisms, m.p. 200 °C (decomp.) (Found: C, 34.1; H, 3.9; N, 15.8; S, 8.8. $C_{10}H_{13}IN_4S$ requires C, 34.5; H, 3.8; N, 16.1; S, 9.2%); $\nu_{max.}$ 1 620 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 0.00 (2 H, s, CH), 2.31 (2 H, s, CH), 7.19 (3 H, s, SMe), and 7.42 (6 H, s, CMe); *m/e* 221 ($M^{\cdot+}$ − I), 206 ($M^{\cdot+}$ − MeI).

Reactions of 4-*Chloro*-2,6-*dimethyl*-1-(1,2,4-*triazol*-4-*yl*)-*pyridinium Tetrafluoroborate* (35).—(a) *With methanol*. Compound (35) (2.9 g) and $NaBH_4$ (0.3 g) in MeOH (10 ml) were heated under reflux (4 h). After cooling, the solid which separated was recrystallised from MeOH to give 4-*methoxy*-2,6-*dimethyl*-1-(1,2,4-*triazol*-4-*yl*)*pyridinium tetrafluoroborate* (39; R = Me) (1.4 g, 50%), prisms, m.p. 200—202 °C (Found: C, 40.7; H, 4.8; N, 19.0. $C_{10}H_{13}BF_4N_4O$ requires C, 41.1; H, 4.5; N, 19.1%); $\lambda_{max.}$ 275 nm (ε 13 400); $\nu_{max.}$ 1 000—1 100br cm^{-1} (BF_4^-); τ ($CF_3{\cdot}CO_2H$) 0.24 (2 H, s, CH), 2.52 (2 H, s, CH), 5.70 (3 H, s, OMe), and 7.44 (6 H, s, CMe); *m/e* 205 ($M^{\cdot+}$ − BF_4).

(b) *With ethanol*. Compound (35) (2.9 g) and $MeNH_2$ (5 ml) in EtOH (10 ml) were heated under reflux (4 h). After cooling, the solid which separated was recrystallised from EtOH to give 4-*ethoxy*-2,6-*dimethyl*-1-(1,2,4-*triazol*-4-*yl*)-*pyridinium tetrafluoroborate* (39; R = Et) (1.5 g, 50%), prisms, m.p. 208—210 °C (Found: C, 42.8; H, 4.8; N, 18.1. $C_{11}H_{15}BF_4N_4O$ requires C, 43.1; H, 4.9; N, 18.3%); $\lambda_{max.}$ 215 (ε 5 700) and 260 nm (12 400); $\nu_{max.}$ 1 000—1 100br cm^{-1} (BF_4^-); τ ($CF_3{\cdot}CO_2H$) 0.32 (2 H, s, CH), 2.63 (2 H, s, CH), 5.46 (2 H, q, OCH_2, *J* 7 Hz), 7.49 (6 H, s, CMe), and 8.40 (3 H, t, $CH_2{\cdot}CH_3$, *J* 7 Hz); *m/e* 219 ($M^{\cdot+}$ − BF_4).

(c) *With aniline*. Compound (35) (2.9 g) and aniline (0.9 g) in EtOH (10 ml) were stirred (1 h). The solid which separated was recrystallised from EtOH to give 2,6-*dimethyl*-4-*phenylamino*-1-(1,2,4-*triazol*-4-*yl*)*pyridinium tetrafluoroborate* (36) (2.5 g, 70%), prisms, m.p. 232—235 °C (Found: C, 50.8; H, 4.9; N, 19.7. $C_{15}H_{16}BF_4N_5$ requires C, 51.0; H, 4.5; N, 19.8%); $\lambda_{max.}$ 300 nm (ε 12 600); $\nu_{max.}$ 3 300 (NH) and 1 000—1 100br cm^{-1} (BF_4^-); τ ($CF_3{\cdot}CO_2H$) 0.30 (2 H, s, CH), 1.00 (s, NH), 2.3—2.8 (5 H, m, Ph), 2.91 (s, CH), 3.15 (s, CH), 7.66 (3 H, s, CMe), and 7.76 (3 H, s, CMe); *m/e* 266 ($M^{\cdot+}$ − BF_4).

The salt (36) (3.5 g) in EtOH (20 ml) was heated at 50 °C

(1 h) with KOH (0.56 g). After cooling, water (20 ml) was added and the solution extracted with $CHCl_3$. Evaporation of the dry extract gave a solid which was recrystallised from EtOH to give 2,6-*dimethyl*-4-*phenylimino*-1-(1,2,4-*triazol*-4-*yl*)-4-*pyridone* (40) (1.6 g, 60%), prisms, m.p. 222—225 °C (Found: C, 67.6; H, 5.6; N, 26.1. $C_{15}H_{15}N_5$ requires C, 67.9; H, 5.7; N, 26.4%); $\lambda_{max.}$ 287 nm (ε 11 000); $\nu_{max.}$ 1 655 cm^{-1} (C=N); τ 1.6 (2 H, s, CH), 2.5—3.3 (5 H, m, Ph), 3.81 (s, CH), 4.02 (s, CH), 8.16 (3 H, s, CMe), and 8.29 (3 H, s, CMe); *m/e* 265 ($M^{\cdot+}$), 197, and 182, *m** 147 (265 ⟶ 197), *m** 168 (197 ⟶ 182).

(d) *With thiourea.* Compound (35) (1.15 g) and thiourea (0.76 g) in EtOH (10 ml) were heated under reflux (4 h). A solution of NaOH in EtOH (5%; 20 ml) was then added and the solution was heated again at reflux temperature (4 h). After cooling, water (20 ml) was added; the solid which separated was 2,6-dimethyl-1-(1,2,4-triazol-4-yl)-pyridine-4-thione (34), m.p. 170—173 °C, identical with an authentic sample (described above).

(e) *With dimethylamine.* Compound (35) (2.9 g), Me_2NH (0.7 g), and EtOH (25 ml) were heated until all the solid had dissolved (*ca.* 1 h). The hot solution was filtered and upon cooling a crystalline solid separated. Recrystallisation from EtOH gave 2,6-*dimethyl*-4-*dimethylamino*-1-(1,2,4-*triazol*-4-*yl*)*pyridinium tetrafluoroborate* (33; R = Me) (60%), as tiny cream crystals, m.p. 240 °C (decomp.) (Found: C, 42.9; H, 5.7; N, 23.1. $C_{11}H_{16}BF_4N_5$ requires C, 43.3; H, 5.3; N, 23.0%); $\lambda_{max.}$ 230 (ε 4 800) and 295 nm (12 400); $\nu_{max.}$ 1 640 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 0.31 (2 H, s, CH), 3.12 (2 H, s, CH), 6.58 (6 H, s, NMe), and 7.64 (6 H, s, CMe); *m/e* 218 ($M^{\cdot+}$ − BF_4).

Using a similar procedure the following compounds were prepared from compound (35) (0.01 mol) and the appropriate secondary amine (0.015 mol) and recrystallised from EtOH.

(i) *From pyrrolidine to give* 2,6-*dimethyl*-4-*pyrrolidino*-1-(1,2,4-*triazol*-4-*yl*)*pyridinium tetrafluoroborate* (33; NR_2 = pyrrolidino) (70%), as a cream powder, m.p. 200 °C (decomp.) (Found: C, 45.7; H, 5.7; N, 20.2. $C_{13}H_{18}BF_4N_5{,}0.5H_2O$ requires C, 45.9; H, 5.6; N, 20.6%); $\lambda_{max.}$ 230 (ε 6 000) and 297 nm (14 800); $\nu_{max.}$ 1 640 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 0.25br (2 H, s, CH), 3.23 (2 H, s, CH), 6.25 (4 H, m, CCH_2), and 7.60 (10 H, m, NCH_2 + CMe).

(ii) *From piperidine to give* 2,6-*dimethyl*-4-*piperidino*-1-(1,2,4-*triazol*-4-*yl*)*pyridinium tetrafluoroborate* (33; NR_2 = piperidino) (70%), as yellow prisms, m.p. 240—241 °C (Found: C, 48.5; H, 5.7; N, 20.0. $C_{14}H_{20}BF_4N_5$ requires C, 48.7; H, 5.8; N, 20.3%); $\lambda_{max.}$ 231 (ε 5 400) and 298 nm (14 100); $\nu_{max.}$ 1 640 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 2.50 (2 H, s, CH), 3.03 (2 H, s, CH), 6.17 (4 H, m, NCH_2), 7.66 (6 H, s, CMe), and 8.10 (6 H, m, CCH_2).

(iii) *From morpholine to give* 2,6-*dimethyl*-4-*morpholino*-1-(1,2,4-*triazol*-4-*yl*)*pyridinium tetrafluoroborate* (33; NR_2 = morpholino) (70%), tiny pale yellow crystals, m.p. 253—256 °C (Found: C, 44.4; H, 5.1; N, 19.8. $C_{13}H_{18}BF_4N_5O$ requires C, 44.9; H, 5.2; N, 20.2%); $\lambda_{max.}$ 232 (ε 3 200) and 300 nm (7 600); $\nu_{max.}$ 1 640 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 0.29 (2 H, s, CH), 2.90 (2 H, s, CH), 5.90 (8 H, m, $NCH_2{\cdot}CH_2O$), and 7.58 (6 H, s, Me).

(iv) *From* N-*methylaniline to give* 2,6-*dimethyl*-4-(N-*methylanilino*)-1-(1,2,4-*triazol*-4-*yl*)*pyridinium tetrafluoroborate* (33; NR_2 = NMePh) (60%), needles, m.p. 232—234 °C (Found: C, 52.1; H, 4.8; N, 19.0. $C_{16}H_{18}BF_4N_5$ requires C, 52.3; H, 4.9; N, 19.1%); $\lambda_{max.}$ 245 (ε 12 000) and 297 nm (7 000); $\nu_{max.}$ 1 650 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 2.50 (2 H, s, CH), 2.2—2.8 (5 H, m, Ph), 2.84 (1 H, d, CH, *J* 3 Hz), 3.49 (1 H, d, CH, *J* 3 Hz), 6.30 (3 H, s, NMe), 7.53 (3 H, s, CMe), and 7.80 (3 H, s, CMe); *m/e* 280 ($M^{\cdot+}$ − BF_4).

4-*Dicyanomethylene*-2,6-*dimethyl*-1-(1,2,4-*triazol*-4-*yl*)-4-*pyridone* (38; X = CN).—Compound (39; R = Me) (2.9 g) and malononitrile (0.66 g) in EtOH (20 ml) were heated under reflux (4 h). After cooling, ice (5 g) was added and the solid which separated was recrystallised from glacial acetic acid to give compound (38; X = CN) (0.5 g, 22%), m.p. 278—280 °C, identical with an authentic sample (described above).

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