Synthesis, Spectroscopic Properties, and Chemistry of 4,6-Diphenyl-2-pyridones and 4,6-Diphenylpyridine-2-thiones and their Relationship to Isomeric Species [1]

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4,6-Diphenylpyran-2-imines (9) are rearranged by sodium ethoxide to the isomeric 2-pyridones (10), but the corresponding thiopyran-2-imines (21) do not rearrange to pyridine-2-thiones (25). The conversion (10) ⟶ (25) is effected by phosphorus pentasulphide. Certain pyridine-2-thiones (25) rearrange to 2-arylthiopyridines (27) on heating. The isomeric compounds are readily distinguished by their mass spectra: n.m.r., u.v., and i.r. spectra are discussed.

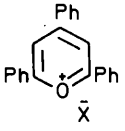
In connection with our interest in the use of 2,4,6-triphenylpyrylium salts (1) as reagents for organic synthesis,[2] we have extended our studies to the chemistry of 4,6-diphenyl-2-pyrone (2; X = O) and related species.[1b] The preparation of the 2-pyrone (2; X = O) [3,4] and its monothio- [(2; X = S) and (3; X = O)] [4,5] and dithio-

[1] (*a*) *N*-Oxides and Related Compounds, Part 57. Part 56, A. S. Afridi, A. R. Katritzky, and C. A. Ramsden, preceding paper; (*b*) A. S. Afridi, A. R. Katritzky, and C. A. Ramsden, *J.C.S. Chem. Comm.*, 1976, 899.

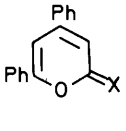
[2] J. B. Bapat, R. J. Blade, A. J. Boulton, J. Epsztajn, A. R. Katritzky, J. Lewis, P. Molina-Buendia, P.-L. Nie, and C. A. Ramsden, *Tetrahedron Letters*, 1976, 2691.

[3] E. P. Kohler and L. L. Steele, *J. Amer. Chem. Soc.*, 1919, **41**, 1093; E. P. Kohler, *ibid.*, 1922, **44**, 379; F. Arndt and B. Eistert, *Ber.*, 1925, **58B**, 2318.

analogues (3; X = S) [4-7] have been reported by earlier workers and some reactions of these compounds (or their methiodides) with primary amines or hydrazines have been described.[4-6] The reactions can in principle lead to 2-pyridone derivatives (4; X = O) and pyridine-2-thione derivatives (4; X = S) or to the isomeric imine derivatives (5; X = O or S). In practice the structure of the product appears to depend on the nature of the



(1)



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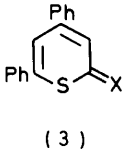

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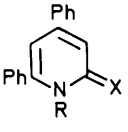

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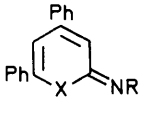
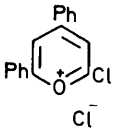


(5)

heterocycle [(2) or (3); X = O or S], the type of nucleophile, and the reaction conditions. For example, 4,6-diphenyl-2-pyrone (2; X = O) and 4,6-diphenylthiopyran-2-one (3; X = O) react with various primary aliphatic amines giving 4,6-diphenyl-2-pyridones (4; X = O).[4,5] In contrast, reaction of the 2-pyrone (2; X = O) with aromatic amines in the presence of phosphoryl chloride gives products which have been assigned the general imine structure (5; X = O).[8] In the case of the 4,6-diphenylthiopyran-2-thione (3; X = S), or its methiodide, reaction with a variety of primary amino-compounds appears to give exclusively products with the imine-type structure (5; X = S);[5,6] the isomeric pyridine-2-thiones (4; X = S) are not available *via* this route. Similarly, the pyran-2-thione (2; X = S) reacts with phenylhydrazine giving a product which is reported to have the hydrazone structure (5; X = O, R = NHPh).[4] However, the same compound (2; X = S) reacts with

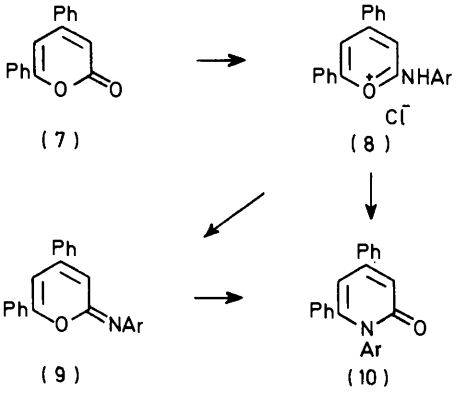


(6)

methylamine giving the pyridine-2-thione (4; X = S, R = Me).[4]

To establish firmly the relationship between pairs of isomers of the general types (4) and (5), we now report general preparative routes to pairs of isomers of this general structure [(4) and (5)], some interconversions of these structural types, and their unambiguous structure determination by mass spectrometry and by chemical transformations.

4,6-Diphenylpyran-2-imines (9) *and* *4,6-Diphenyl-2-pyridones* (10).—Van Allan and Chang [8] have reported that 4,6-diphenyl-2-pyrone (7) reacts with aniline or 2,4-dinitroaniline in the presence of phosphoryl chloride giving the pyran-2-imines [9; Ar = Ph or $(NO_2)_2C_6H_3$]. In this reaction, the 2-chloropyrylium cation (6) is

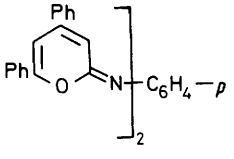


(7) (8) (9) (10)

a; Ar = phenyl
b; Ar = *o*-tolyl
c; Ar = *p*-tolyl
d; Ar = *p*-chlorophenyl
e; Ar = 2-pyridyl
f; Ar = 5-methyl-2-pyridyl
g; Ar = 4-methyl-2-pyridyl
h; Ar = 3-methyl-2-pyridyl

SCHEME 1

presumably a reactive intermediate. Since this procedure provides a potential synthetic route to the 2-pyridones (10), we have re-examined the reaction in some detail. In our hands, the reaction of 4,6-diphenyl-2-pyrone (7) with aromatic amines in phosphoryl chloride at reflux temperature gave yellow crystalline 2-arylamino-4,6-diphenylpyrylium chlorides (8) in 60—80% yield.



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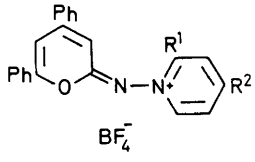

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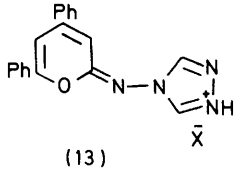

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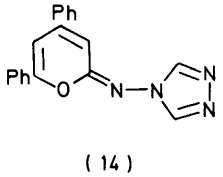


(14)

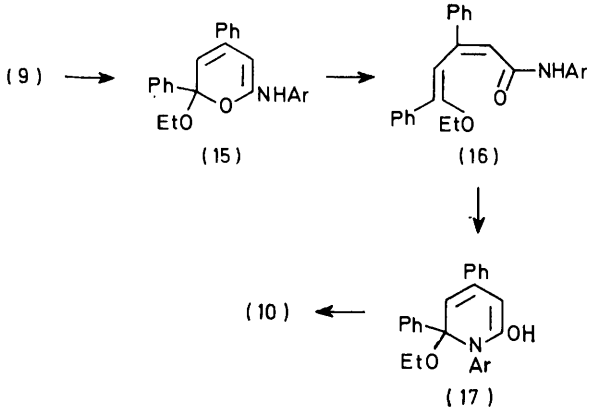
Using this method, the chlorides (8a—h) were prepared; their structures are fully supported by elemental analyses and spectroscopic properties. The chlorides (8) can be converted into the free imines (9) by recrystallisation from pyridine–methanol. Using *p*-phenylenediamine, the bis-imine (11) was isolated directly by recrystallisation of the crude product from pyridine.

In a similar sequence, compound (7) reacted with

[4] I. E.-S. El-Kholy, F. K. Rafla, and M. M. Mishrikey, *J. Chem. Soc.* (*C*), 1970, 1578.
[5] J. Faust, G. Speier, and R. Mayer, *J. prakt. Chem.*, 1969, **311**, 61.
[6] H. Behringer and A. Grimm, *Annalen*, 1965, **682**, 188.
[7] R. Mayer and J. Wehl, *Angew. Chem. Internat. Edn.*, 1965, **4**, 246.
[8] J. A. Van Allan and S. C. Chang, *J. Heterocyclic Chem.*, 1974, **11**, 1065.

N-aminopyridines giving *NN'*-pyridinium-2-iminopyrones (12). Thus, *N*-aminopyridinium chloride gave a salt which upon treatment with tetrafluoroboric acid yielded the *N*-pyran-2-ylideneaminopyridinium tetrafluoroborate (12; $R^1 = R^2 = H$) and in the same way, from *N*-amino-2- or -4-pyridone, the chloro-derivatives (12; $R^1 = Cl$, $R^2 = H$) and (12; $R^1 = H$, $R^2 = Cl$) were obtained. Using 4-amino-1,2,4-triazole, the chloride (13; X = Cl) was isolated as yellow prisms, and treatment of this salt with tetrafluoroboric acid gave the tetrafluoroborate (13; $X = BF_4$). In an alternative work-up, recrystallisation of the chloride (13; X = Cl) from aqueous ethanol gave the free base (14).

The spectroscopic properties of the imines (9), (11), and (14) and the salts (8), (12), and (13) are entirely consistent with the proposed structures, but on the basis of their absorption spectra alone it is not possible to eliminate the isomeric 2-pyridone structures [*e.g.* (10)]. However, an analysis of their mass spectral fragmentation patterns and a study of their chemical transformations firmly establishes their consititutional formulae. A



SCHEME 2

detailed comparative analysis of the mass spectra of the imines (9) is given in a later section: the observation of a molecular ion and the fragment $PhC{\equiv}O^+$ (*m/e* 105) provides unambiguous structural information. Furthermore, the chlorides (8) are readily transformed into the *N*-aryl-2-pyridone derivatives (10) by hot ethanolic sodium ethoxide. Typically the yellow crystalline chloride (8a) dissolves in the ethanolic solution giving an immediate red colouration which slowly fades to yellow and then disappears over 12 h at reflux temperature. The yield of the pyridone is 80% and in a similar manner the derivatives (10b—h) were also prepared. This procedure provides a convenient route to *N*-arylpyridones.

The primary product of this base-catalysed reaction (8) ⟶ (10) is probably the free imine (9); in a separate experiment 4,6,*N*-triphenylpyran-2-imine (9a) rearranged in hot ethanolic sodium ethoxide to 1,4,6-triphenyl-2-pyridone (10a) in 60% yield. This rearrangement (9) ⟶ (10) presumably involves the initial addition of ethanol to give the intermediate (15), which then undergoes an electrocyclic ring opening to afford the unsaturated amide (16) (Scheme 2). Recyclisation and elimination of ethanol (16) ⟶ (17) ⟶ (10) then gives the thermodynamically more stable pyridone (10) (Scheme 2). A similar rearrangement of pyran-2-thiones [(2; X = S) ⟶ (3; X = O)] in the presence of methanolic dimethylamine has been reported.[4] These rearrangements of the general types (2; X = NR) ⟶ (4; X = O) and (2; X = S) ⟶ (3; X = O) in alcoholic solution are closely related to similar rearrangements of isoelectronic mesoionic systems.[9]

The *N*-aryl-2-pyridones (10) are distinct from the isomeric imines (9) and their chlorides (8). Their u.v. and visible spectral characteristics are exemplified by those of the triphenyl derivatives (9a) [$\lambda_{max.}$ 215 (ε 6 200), 275 (13 200), and 395 nm (4 000)] and (10a) [$\lambda_{max.}$ 220 (ε 11 400), 250 (13 400), and 337 nm (4 800)]; the orange or red imines (9) absorb at longer wavelength than the colourless 2-pyridones (10). The i.r. spectra of the 2-pyridones (10) show an absorption (1 655—1 675 cm^{-1}) which can be attributed to the C=O stretching vibration, but this assignment is not unambiguous since the imines (9) and their chlorides (8) also absorb in this region (1 650—1 665 cm^{-1}). Similarly, the n.m.r. spectra of the 2-pyridones (10) support their constitution but cannot eliminate the isomeric imine structure (9).

The mass spectra of the *N*-aryl-2-pyridones (10) show informative fragment ions which clearly distinguish them from the isomers (9). Significantly, no fragment ion at *m/e* 105 ($PhC{\equiv}O^+$) is observed. Furthermore, the observation of molecular ions and fragment ions at *m/e* 103 ($PhC{\equiv}N^{+\cdot}$) and *m/e* 104 ($PhC{\equiv}NH^+$) provides powerful support for the 2-pyridone structure (10). The mass spectral fragmentation pattern is discussed in detail in a later section.

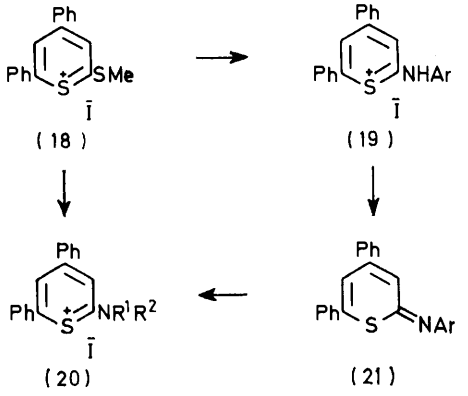
4,6-Diphenylthiopyran-2-imines (21) *and 4,6-Diphenylpyridine-2-thiones* (25).—2-Methylthio-4,6-diphenylthiopyrylium iodide (18), easily prepared [5] by methylation of the thiopyranthione (3; X = S), reacts with primary amines giving products which have been formulated as either the thiopyranimines (21) or their iodides (19).[5] We have now employed this procedure to prepare a number of thiopyranimines (21) from aromatic amines. In a typical reaction, the iodide (18) was fused at its m.p. with 1 equiv. of the appropriate aromatic amine, and after heating in ethanol at reflux temperature, the 2-aminothiopyrylium iodide (19) was obtained in yields of 50—70%. Using this method we have obtained the salts (19a—h) as orange-brown crystals. Their i.r. spectra show absorptions in the region 1 610—1 635 cm^{-1} which can be attributed to C=N stretching vibrations; their n.m.r. spectra show an NH signal at low field together with signals attributable to the aryl substituents.

Treatment of ethanolic solutions of the iodides (19) with sodium ethoxide did not result in rearrangement to pyridine-2-thiones (25). Instead, deprotonation occurred giving the free imines (21b, c, and f—h) in good

[9] W. D. Ollis and C. A. Ramsden, *Adv. Heterocyclic Chem.*, 1976, **19**, 1; R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *J.C.S. Chem. Comm.*, 1976, 306; E. Cawkill, W. D. Ollis, and C. A. Ramsden, and G. P. Rowson, *ibid.*, p. 439.

yield. The spectroscopic properties of these imines (21) are similar to those of the corresponding oxygen derivatives (9) and, although not conclusive, do support their constitution (21).

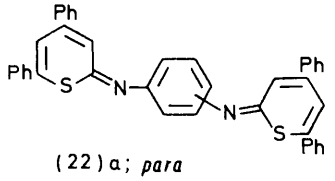
We have also treated the iodide (18) with various other



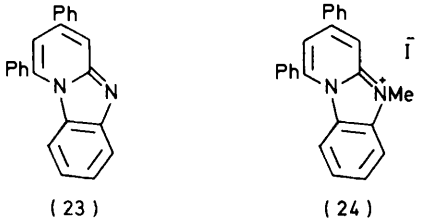
a; Ar = phenyl
b; Ar = *o*-tolyl
c; Ar = *p*-tolyl
d; Ar = *m*-nitrophenyl
e; Ar = 2-pyridyl
f; Ar = 5-methyl-2-pyridyl
g; Ar = 4-methyl-2-pyridyl
h; Ar = 3-methyl-2-pyridyl
i; $R^1 = R^2 = Me$
j; $R^1 = Me$, $R^2 = Ph$
k; NR^1R^2 = pyrrolidin-1-yl
l; NR^1R^2 = piperidino
m; NR^1R^2 = morpholino
n; Ar = 1,2-dihydro-2-oxo-1-pyridyl
o; Ar = 1,2,4-triazol-4-yl
p; Ar = PhCO·NH

SCHEME 3

amine derivatives. Treatment with secondary amines, using the procedure described for primary aromatic amines, gave good yields of the thiopyrylium iodides (20), and in this manner the salts (20i—m) were obtained. Compound (20j) prepared by this method was identical



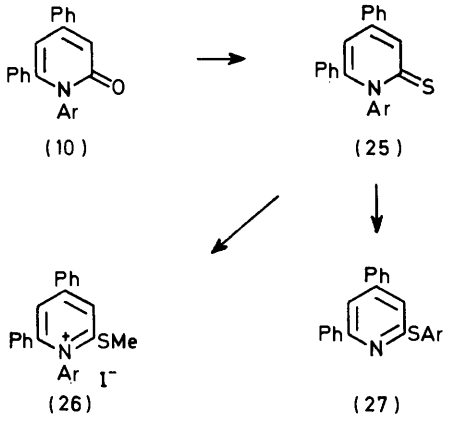
(22) a; *para*
b; *meta*



with a sample prepared by Menschutkin methylation of the imine (21a) using methyl iodide. These two routes to compound (20j) provide unambiguous evidence for the imine constitution (21).

Using *N*-amino-2-pyridone and 4-amino-1,2,4-triazole the imines (21n) and (21o) were obtained without isolation of the intermediate iodides. Similarly *m*- and *p*-phenylenediamine gave the bis-thiopyran derivatives (22a and b). Using *o*-phenylenediamine, the pyridobenzimidazole (23) was obtained, and treatment of this product (23) with methyl iodide gave the salt (24).

The failure of the thiopyrylium iodides (19) to rearrange to pyridine-2-thiones (25) in a manner analogous to the transformation (8) ⟶ (10) (Scheme 1) was disappointing since this would have provided a particularly good synthetic route to pyridine-2-thiones (25). The reason for this difference in reactivity of the pyrylium chlorides (8) and the thiopyrylium iodides (19) is not clear, but could well be a reflection of the greater thermodynamic stability of the thiopyrylium cation relative to its oxygen analogue; quite small energy differences (3—5 kcal mol^{-1}) can have profound effects on chemical equilibria. We have been able to prepare pyridine-2-thiones (25) by an alternative route involving treatment



In formulae (25)—(27)
a; Ar = 2-pyridyl
b; Ar = 5-methyl-2-pyridyl
c; Ar = 4-methyl-2-pyridyl
d; Ar = 3-methyl-2-pyridyl
e; Ar = *p*-tolyl

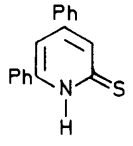
SCHEME 4

of 2-pyridones (10) with phosphorus pentasulphide in pyridine. Using this method the yellow, crystalline pyridine-2-thiones (25a, b, and e) were prepared and fully characterised. They are distinct from the isomeric molecules (21). The i.r. spectra show a clear C=S stretching band at 1 165—1 170 cm^{-1} and their u.v. and visible spectra are distinct from, although similar to, those of the isomers (21), having three absorption bands. Additional support for the structures (25) is provided by their elemental analysis, their n.m.r. spectra, and their mass spectral fragmentation patterns (see later). Furthermore, compounds (25a, b, and e) are readily converted into their methiodides (26a, b, and e) using methyl iodide. The mode of preparation of these pyridine-2-thiones (25) and their spectroscopic properties and chemical transformations firmly establish their constitutional structure, and hence provides rigorous

proof of structure of the precursors (10) and (8) and the isomers (21).

During the preparation of the compounds (25a, b, and e), two other products were isolated in low yield; these have been shown to be the unsubstituted pyridine-2-thione (28) (5—20%) and the corresponding disulphide (29) (5—25%). The formation of (28) must involve the reductive cleavage of the pyridine-2-thiones (25). Examples of phosphorus pentasulphide acting as a reducing agent are known, although the mechanism is uncertain.[10] The disulphide (29) is almost certainly formed by aerial oxidation of the pyridine-2-thione (28). We have achieved this transformation (28) ⟶ (29) using iron(III) chloride as oxidising agent.

A fourth product isolated during the preparation of compound (25b) was the isomeric thioether (27b) (5%). This compound is clearly different from its isomer (25b) and its structure is fully supported by its elemental analysis and spectral properties. Notably, the u.v. spectrum closely resembles that of the disulphide (29).



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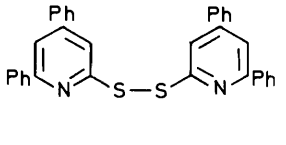


(29)

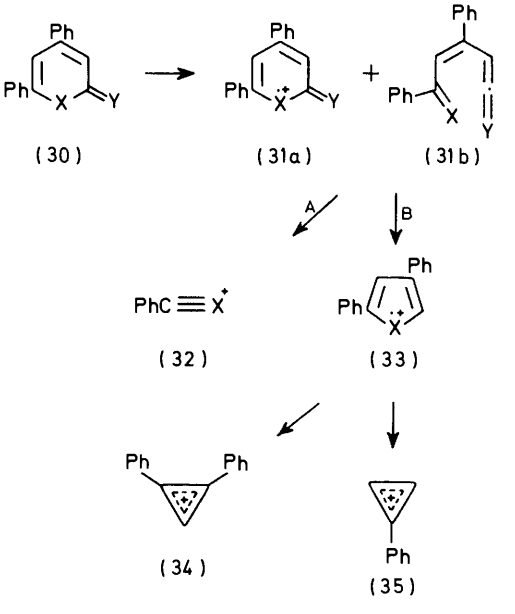
Compound (27b) is formed by a Chapman rearrangement of the pyridine-2-thione (25b). This rearrangement is strikingly demonstrated by the observation that when a pure sample of the pyridine-2-thione (25b) is heated at 210—230 °C for 10 min the thioether (27b) is formed in 40% yield. As might be expected, this rearrangement (25) ⟶ (27) was not successful in the case of the *N*-*p*-tolyl derivative (25e); the *o*-pyridyl function, or a similarly activating substituent, is clearly necessary to facilitate this migration.

Attempts to isolate and characterise the pyridine-2-thiones (25c and d) by treatment of the corresponding 2-pyridones (10) with phosphorus pentasulphide were not successful. In each case, high yields of the undesired by-products (28) (20—30%) and (29) (20%) were obtained, and in the case of the 5-methyl-2-pyridyl derivative the Chapman rearrangement product (27c) was also obtained, in 20% yield.

Mass Spectral Fragmentation of Compounds of General Structure (30).—The fragmentation patterns of all the compounds we have studied are quite simple. The molecular ion (31) (Scheme 5) can be regarded as fragmenting by two major pathways (A and B; Scheme 5). Pathway A gives the daughter ion $PhC{\equiv}X^+$ (32) which is highly diagnostic of the heteroatom in the ring. Pathway B is associated with loss of a C=Y fragment giving a daughter ion (33) which we have represented by a five-membered cyclic structure. This type of cleavage (pathway B) clearly identifies the exocyclic heteroatom (Y). Further fragmentation of (33) accounts for the observation of the cyclopropenium cations (34) and (35), although ions corresponding to this constitution could be formed directly from the molecular ion (31).

In the case of the nitrogen-containing species (30; X or Y = NR), an additional fragmentation of the molecular ion (31; X or Y = NR) is observed, corresponding to a simple loss of the nitrogen substituent ($\dot{R}N^+{-}Ar \longrightarrow RN^+ + A\dot{r}$). The resulting daughter ions then appear to fragment in the usual manner (Scheme 5; X or Y = N).

Spectra of 4,6-*Diphenyl*-2-*pyrone* (7) *and its Sulphur Analogues*.—The mass spectra of these four diphenyl derivatives (7) and (36)—(38) are shown in Figure 1. All these compounds show a strong molecular ion peak and an intense fragment ion peak corresponding to the loss of either CO or CS from the molecular ion (pathway B; Scheme 5). Further fragmentation gives the phenylcyclopropenium ion (35; Scheme 5) (*m/e* 115) and the diphenylcyclopropenium ion (34; Scheme 5) (*m/e* 191). In addition, the 2-thiones (36) and (38) are associated with a weak ion which can be attributed to loss of SH· from the molecular ion. Fragmentation by pathway A



(30) (31a) (31b) (32) (33) (34) (35)

SCHEME 5

(Scheme 5) is observed in all the spectra (Figure 1) but the intensity of the daughter ion peak ($PhC{\equiv}X^+$) is variable. The pyran derivatives (7) and (38) give the ion $PhC{\equiv}O^+$ (*m/e* 105) whereas the thiopyran derivatives (36) and (37) give the ion $PhC{\equiv}S^+$ (*m/e* 121) and this provides a valuable method of distinguishing between isomeric structural types [*e.g.* (37) and (38)].

Spectra of 1,4,6-*Triaryl*-2-*pyridones* (10), 4,6-*Diphenylpyran*-2-*imines* (9), *and their Sulphur Analogues* (21) *and* (25).—The mass spectra of two pairs of isomers of the types [(9) and (10)] and [(21) and (25)] are shown in Figure 2; these spectra are representative of all the derivatives which we have studied. The fragmentation

[10] K. T. Potts and D. McKeough, *J. Amer. Chem. Soc.*, 1974, **96**, 4268.

pattern of the isomers (39) and (40) (Figure 2) clearly shows that mass spectrometry unambiguously differentiates between these two structural types. In the spectra of both compounds (39) and (40), the base peak is the molecular ion (*m/e* 323). Both molecular ions lose the *N*-phenyl substituent giving a weak daughter ion peak at *m/e* 246, and similarly both spectra show strong peaks at *m/e* 191 and 115 corresponding to the cyclopropenium structures (34) and (35) shown in Scheme 5 (pathway B). However, whereas compound (39) gives a strong fragment peak at *m/e* 220 corresponding to the loss of PhN=C (pathway B; Scheme 5), a similar fragmentation of the isomer (40) is associated with loss of carbon monoxide and gives an intense peak at *m/e* 295. Also significant is the appearance of a moderately intense peak at *m/e*

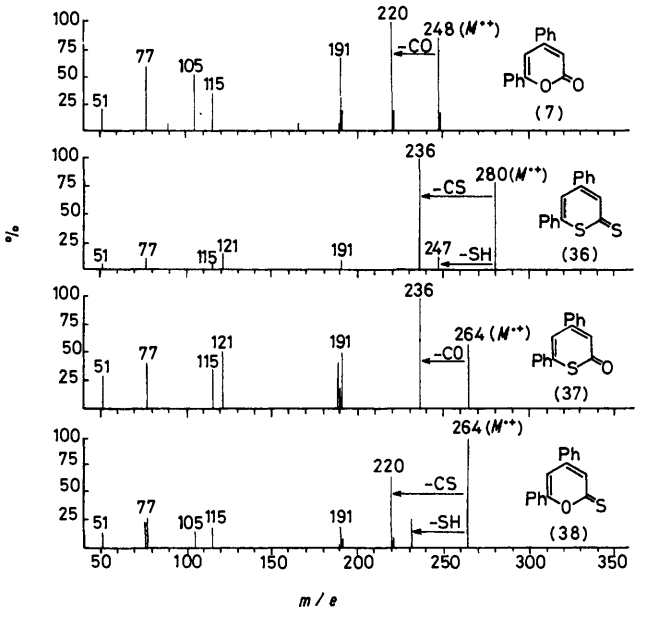


FIGURE 1 Comparison of the mass spectra of 4,6-diphenyl-2-pyrone (7) and its sulphur analogues (36)—(38)

105 ($PhC{\equiv}O^+$) in the spectrum of compound (39) (pathway A; Scheme 5); this ion ($PhC{\equiv}O^+$) is absent from the spectrum of the isomer (40).

The mass spectrum of the thiopyranimine (41) (Figure 2) is also easily rationalised in terms of the general fragmentation pattern shown in Scheme 5. Particularly important is the ion at *m/e* 121 ($PhC{\equiv}S^+$), which immediately distinguishes it from the isomeric pyridine-2-thione (42).

The mass spectra of the pyridine-2-thiones (25) are not so straightforward and we rationalise the spectrum of compound (42) (Figure 2) in terms of an initial isomerisation of the molecular ion to a thioether (Scheme 6). This process (25) ⟶ (43) (Scheme 6) could take place thermally in the probe of the mass spectrometer or alternatively it may be activated by electron impact. We have already demonstrated similar thermal rearrangements of 2-pyridyl derivatives [(25b and c) ⟶ (27b and c)] in an earlier section of this paper. The pyridinethione structure (42) is fully supported by the observation of an intense molecular ion peak (*m/e* 353) but, in contrast to the spectra of the other thione derivatives (36) and (38) (Figure 1) which we have studied, the thiopyridone (42) shows only very weak fragment ion peaks (*ca.* 5%) corresponding to loss of SH and CS

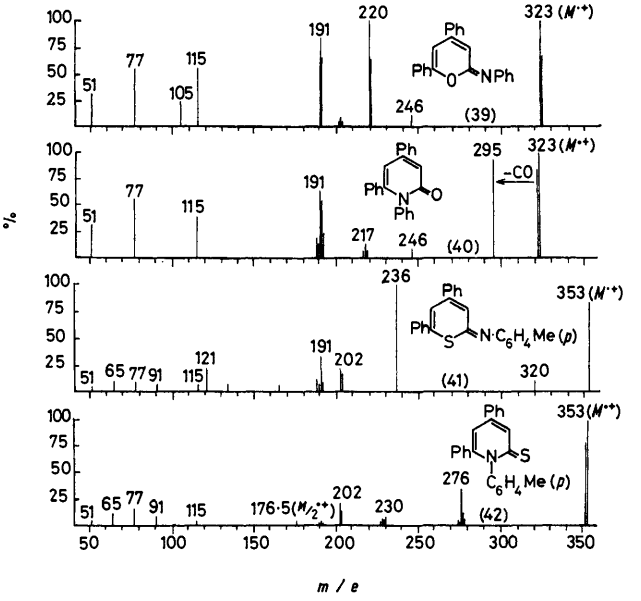
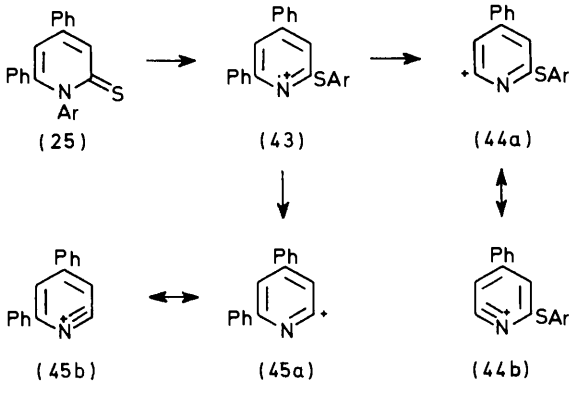


FIGURE 2 Comparison of the mass spectra of the pyran-2-imine (39), the 2-pyridone (40), the thiopyran-2-imine (41), and the pyridine-2-thione (42)

from the molecular ion. Also unusual is the observed loss of phenyl radical from the molecular ion giving a daughter ion at *m/e* 276. However, here it is significant that the mass spectra of the authentic thioethers (27) show a loss of the phenyl radical from their molecular ion and this type of fragmentation can be rationalised by the



SCHEME 6

process (43) ⟶ (44) (Scheme 6). Furthermore, the mass spectrum of compound (42) shows a fragment ion at *m/e* 230 corresponding to the loss of *p*-MeC_6H_4S from the molecular ion; this fragmentation is readily accounted for in terms of a cleavage of an intermediate diaryl sulphide [(43) ⟶ (45)] (Scheme 6). The remaining features of the spectrum of compound (42) (Figure 2)

can be rationalised in terms of previously discussed fragment ions.

EXPERIMENTAL

Unless otherwise stated, i.r. spectra were measured for Nujol mulls, u.v. spectra for solutions in EtOH, and n.m.r. spectra (60 MHz) for solutions in $CDCl_3$ (Me_4Si as internal reference). Only significant bands from i.r. spectra are quoted. Evaporation refers to the removal of volatile materials under diminished pressure. When substances are stated to be identical, this refers to their m.p.s and comparative i.r. and n.m.r. spectra. The mass spectra were recorded on a Hitachi–Perkin-Elmer RMU-6E spectrometer (direct inlet system; source temperature 300 °C). An ionising voltage of 75 eV was used.

Preparation of 2-Amino-4,6-diphenylpyrylium Chlorides (8a—h).—4,6-Diphenyl-2-pyrone (7) (0.5 g) [3] and aniline (0.2 g) in $POCl_3$ (15 ml) were heated under reflux (8 h). After cooling, the mixture was extracted with Et_2O (4 × 30 ml) and the extracts discarded. The residual sticky solid was crystallised by stirring with EtOH–Et_2O (20 ml); the crystalline product when washed with Et_2O (2 × 20 ml) gave *2-anilino-4,6-diphenylpyrylium chloride* (8a) (0.56 g, 80%), yellow prisms, m.p. 210—220 °C (decomp.) (Found: C, 76.6; H, 5.1; N, 3.7. $C_{23}H_{18}ClNO$ requires C, 76.8; H, 5.0; N, 3.9%); $\lambda_{max.}$ 220 (ε 5 800), 275 (12 200), and 400 nm (3 400); $\nu_{max.}$ 1 665 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 2.0—2.8 (m, arom. H); *m/e* 323 ($M^{+\cdot}$ − HCl).

In a similar manner the following salts were prepared from the appropriate arylamine: *4,6-diphenyl-2-(o-toluidino)-pyrylium chloride* (8b) (60%), yellow prisms, m.p. 170—172 °C (decomp.) (Found: C, 76.9; H, 5.4; N, 3.8. $C_{24}H_{20}ClNO$ requires C, 77.1; H, 5.4; N, 3.7%); $\lambda_{max.}$ 215 (ε 7 400), 275 (12 000), and 380 nm (3 800); $\nu_{max.}$ 1 660 cm^{-1} (C=N); τ 1.8—3.0 (16 H, m, arom. H) and 7.58 (3 H, s, Me); *m/e* 338 ($M^{+\cdot}$ − ^{35}Cl) and 337 ($M^{+\cdot}$ − HCl); *4,6-diphenyl-2-(p-toluidino)pyrylium chloride* (8c) (70%), yellow prisms, m.p. 167—170 °C (decomp.) (Found: C, 76.8; H, 5.2; Cl, 9.4; N, 3.7. $C_{24}H_{20}ClNO$ requires C, 77.1; H, 5.4; Cl, 9.5; N, 3.8%); $\lambda_{max.}$ 217 (ε 6 000), 280 (12 000), and 400 nm (3 000); $\nu_{max.}$ 1 665 cm^{-1} (C=N); τ 1.5—2.9 (16 H, m, arom. H) and 7.60 (3 H, s, Me); *m/e* 338 ($M^{+\cdot}$ − ^{35}Cl) and 337 ($M^{+\cdot}$ − HCl); *2-(p-chloroanilino)-4,6-diphenylpyrylium chloride* (8d) (70%), yellow prisms, m.p. 220—222 °C (decomp.) (Found: C, 69.7; H, 4.0; N, 3.2. $C_{23}H_{17}Cl_2NO$ requires C, 70.0; H, 4.3; N, 3.5%); $\lambda_{max.}$ 220 (ε 5 000), 278 (11 400), and 400 nm (1 800), $\nu_{max.}$ 1 660 cm^{-1} (C=N); τ 1.8—2.6 (m, arom. H); *m/e* 359 ($M^{+\cdot}$ − ^{35}Cl) and 357 ($M^{+\cdot}$ − HCl); *2-(5-methyl-2-pyridylamino)-4,6-diphenylpyrylium chloride hydrochloride* (8f) (60%), yellow prisms, m.p. 230—232 °C (decomp.) (Found: C, 67.0; H, 5.1; N, 6.8. $C_{23}H_{20}Cl_2N_2O$ requires C, 67.2; H, 4.9; N, 6.8%); $\lambda_{max.}$ 220 (ε 6 800), 282 (11 200), and 420 nm (4 600); $\nu_{max.}$ 1 650 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 1.2—2.6 (15 H, m, arom. H), and 7.30 (3 H, s, Me); *m/e* 338 ($M^{+\cdot}$ − 2HCl); *2-(4-methyl-2-pyridylamino)-4,6-diphenylpyrylium chloride hydrochloride* (8g) (60%), yellow needles, m.p. 228—230 °C (decomp.) (Found: C, 67.0; H, 5.2; N, 7.2. $C_{23}H_{20}Cl_2N_2O$ requires C, 67.2; H, 4.9; N, 6.8%); $\lambda_{max.}$ 215 (ε 5 600), 288 (12 000), and 420 nm (600); $\nu_{max.}$ 1 660 cm^{-1} (C=N); τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 1.3—3.0 (15 H, m, arom. H) and 7.40 (3 H, s, Me); *m/e* 338 ($M^{+\cdot}$ − 2HCl); *2-(3-methyl-2-pyridylamino)-4,6-diphenylpyrylium chloride* (8h) (60%), yellow prisms, m.p. 239—241 °C (decomp.) (Found: C, 73.5; H, 5.1; N, 7.2. $C_{23}H_{19}ClN_2O$ requires C, 73.7; H, 5.1; N, 7.4%); $\lambda_{max.}$ 218 (ε 5 400), 275 (12 400), and 385 nm (3 200); $\nu_{max.}$ 1 650 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 1.0—2.6 (15 H, m, arom. H), and 7.22 (3 H, s, Me); *m/e* 338 ($M^{+\cdot}$ − HCl).

Also prepared was the 2-(2-pyridylamino)pyrylium chloride (8e), which was not characterised but used without further purification.

Preparation of 4,6,N-Triphenylpyran-2-imine (9a).—Recrystallisation of the chloride (8a) from pyridine–MeOH gave compound (9a) (0.32 g, 50%), orange prisms, m.p. 160 °C (lit.,[8] 140 °C) (Found: C, 85.0; H, 5.3; N, 4.1. Calc. for $C_{23}H_{17}NO$: C, 85.4; H, 5.3; N, 4.3%); $\lambda_{max.}$ 215 (ε 6 200), 275 (13 200), and 395 nm (4 000); $\nu_{max.}$ 1 655 cm^{-1} (C=N); τ 2.0—3.7 (m, arom. H); *m/e* 323 ($M^{+\cdot}$).

4,4′,6,6′-Tetraphenyl-NN′-p-phenylenebis(pyran-2-imine) (11).—Compound (7) (0.5 g) and *p*-phenylenediamine (0.19 g) were heated at reflux temperature (4 h) with $POCl_3$ (15 ml). The mixture was washed with Et_2O (3 × 20 ml). The residual viscous solid when crystallised by treatment with EtOH–Et_2O (50 ml; 50%) and recrystallised from pyridine gave *compound* (11) (0.34 g, 60%) as red prisms, m.p. 240 °C (decomp.) (Found: C, 84.2; H, 4.7; N, 5.1. $C_{40}H_{28}N_2O_2$ requires C, 84.5; H, 4.9; N, 4.9%); $\lambda_{max.}$ 220 (ε 9 000), 252 (12 200), 275sh (11 800), and 350 nm (5 800); $\nu_{max.}$ 1 660 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$–Me_2SO) 2.2—3.2 (m, arom. H).

N-(4,6-Diphenylpyran-2-ylideneamino)pyridinium Tetrafluoroborate (12; $R^1 = R^2 = H$).—Compound (7) (0.5 g) and *N*-aminopyridinium chloride (0.24 g) in $POCl_3$ (10 ml) were heated under reflux (8 h). Upon cooling, Et_2O (50 ml) was added. The ethereal solution was decanted and further washing with Et_2O (3 × 20 ml) gave a hygroscopic gum. HBF_4 was then added and the resulting solid was washed with Et_2O and recrystallised from EtOH to give *compound* (12; $R^1 = R^2 = H$) (0.5 g, 60%), prisms, m.p. 210—212 °C (Found: C, 63.8; H, 3.9; N, 6.5. $C_{22}H_{17}BF_4N_2O$ requires C, 64.1; H, 4.1; N, 6.8%); $\lambda_{max.}$ 230 (ε 9 400), 282 (13 500), and 415 nm (4 000); $\nu_{max.}$ 1 050 cm^{-1} (BF_4); τ ($CF_3{\cdot}CO_2H$) 0.7—2.8 (m, arom. H); *m/e* 359 [$M^{+\cdot}(^{35}Cl)$ − BF_4], 246, 191, and 105.

The following derivatives were similarly prepared using 1-amino-2-pyridone, 1-amino-4-pyridone, and 4-amino-1,2,4-triazole: *2-chloro-N-(4,6-diphenylpyran-2-ylideneamino)pyridinium tetrafluoroborate* (12; $R^1 = Cl$, $R^2 = H$) (60%), yellow needles, m.p. 198—200 °C (Found: C, 58.8; H, 4.0; Cl, 7.9; N, 6.5. $C_{22}H_{16}BClF_4N_2O$ requires C, 59.1; H, 3.6; Cl, 8.0; N, 6.3%); $\lambda_{max.}$ 275 (ε 11 000) and 370 nm (3 000); $\nu_{max.}$ 1 050 cm^{-1} (BF_4); τ ($CF_3{\cdot}CO_2H$) 0.8—2.8 (m, arom. H); *m/e* 359 [$M^{+\cdot}(^{35}Cl)$ − BF_4], 245, 191, and 105; *4-chloro-N-(4,6-diphenylpyran-2-ylideneamino)pyridinium tetrafluoroborate* (12; $R^1 = H$, $R^2 = Cl$) (30%), yellow prisms, m.p. 210 °C (decomp.) (Found: C, 58.6; H, 3.3; N, 6.1. $C_{22}H_{16}BClF_4N_2O$ requires C, 59.1; H, 3.6; N, 6.3%); $\lambda_{max.}$ 275 (ε 10 200) and 375 nm (3 000); $\nu_{max.}$ 1 050 cm^{-1} (BF_4); τ ($CF_3{\cdot}CO_2H$) 0.5—3.0 (m, arom. H); *m/e* 359vw [$M^{+\cdot}(^{35}Cl)$ − BF_4] 246, 191, and 105.

4-(4,6-Diphenylpyran-2-ylideneamino)-1,2,4-triazolium tetrafluoroborate (13; X = BF_4). The intermediate *chloride* (13; X = Cl) [(60%), yellow prisms, m.p. 210 °C (decomp.) (Found: Cl, 10.0. $C_{19}H_{15}ClN_4O$ requires Cl, 10.1%); $\lambda_{max.}$ 217 (ε 4 400), 275 (10 000), and 370 nm (2 400); $\nu_{max.}$ 1 655 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 0.3 (2 H, s, CH) and 2.0—2.5 (12 H, m, arom. H)] was treated with HBF_4 to give the *tetrafluoroborate* (13; X = BF_4) (70%), yellow prisms, m.p. 240 °C (decomp.) (Found: C, 57.1; H, 3.5; N, 13.7.

$C_{19}H_{15}BF_4N_4O$ requires C, 56.7; H, 3.7; N, 13.9%); $\lambda_{max.}$ 220 (ε 4 400), 275 (9 800), and 370 nm (2 600); $\nu_{max.}$ 1 660 (C=N) and 1 050 cm^{-1} (BF_4); τ 0.4 (2 H, s, CH) and 2.1—2.6 (12 H, m, arom. H).

In a similar experiment, after washing the chloride (13; X = Cl) with Et_2O, aqueous EtOH was added; the crystalline product was identified as 4-(4,6-*diphenylpyran*-2-*ylideneamino*)-1,2,4-*triazole* (14) (60%), yellow prisms, m.p. 288—290 °C (Found: C, 72.6; H, 4.4; N, 17.7. $C_{19}H_{14}N_4O$ requires C, 72.6; H, 4.5; N, 17.8%); $\lambda_{max.}$ 285 (ε 17 000) and 370 nm (5 600); $\nu_{max.}$ 1 655 cm^{-1} (C=O); τ ($CF_3{\cdot}CO_2H$–Me_2SO) 0.49 (2 H, s, CH), 2.0—2.8 (11 H, m, Ph + CH), and 3.12 (s, CH); *m/e* 314 ($M^{+\cdot}$); identical with a sample prepared from 4,6-diphenylthiopyran-2-thione (2; X = S) as follows. Compound (2; X = S) (2.64 g) and 4-amino-1,2,4-triazole (0.84 g) in pyridine (15 ml) were heated under reflux (12 h). Upon cooling a solid separated which on recrystallisation from EtOH gave compound (14) (60%).

Rearrangement of 2-*Arylamino*-4,6-*diphenylpyrylium Chlorides* (8) *to* 1-*Aryl*-4,6-*diphenyl*-2-*pyridones* (10).—2-Anilino-4,6-diphenylpyrylium chloride (8a) (360 mg, 0.001 mol) and NaOEt (340 mg, 0.005 mol) in EtOH (20 ml) were heated under reflux (10 h). After cooling, water (50 ml) was added to the mixture and the solid product collected and extracted with $CHCl_3$. Evaporation left a residue which was recrystallised from EtOH giving 1,4,6-*triphenyl*-2-*pyridone* (10a) (0.26 g, 80%), needles, m.p. 164—166 °C (Found: C, 85.1; H, 5.3; N, 4.4. $C_{23}H_{17}NO$ requires C, 85.4; H, 5.3; N, 4.3%); $\lambda_{max.}$ 220 (ε 11 400), 250 (13 400), and 337 nm (4 800); $\nu_{max.}$ 1 675 cm^{-1} (C=O); τ 2.1—3.5 (m, arom. H); *m/e* 323 ($M^{+\cdot}$).

The following pyridones were similarly prepared: 4,6-*diphenyl*-1-(o-*tolyl*)-2-*pyridone* (10b) (50%), needles, m.p. 118—120 °C (Found: C, 85.1; H, 5.3; N, 4.2. $C_{24}H_{19}NO$ requires C, 85.5; H, 5.6; N, 4.2%); $\lambda_{max.}$ 225 (ε 8 600), 250 (10 600), and 335 nm (4 000); $\nu_{max.}$ 1 665 cm^{-1} (C=O); τ 1.6—2.5 (16 H, m, arom. H) and 7.21 (3 H, s, Me); *m/e* 337 ($M^{+\cdot}$); 4,6-*diphenyl*-1-(p-*tolyl*)-2-*pyridone* (10c) (72%), needles, m.p. 243—246 °C (Found: C, 85.5; H, 5.7; N, 4.1. $C_{24}H_{19}NO$ requires C, 85.5; H, 5.6; N, 4.2%); $\lambda_{max.}$ 223 (ε 11 000), 250 (12 000), and 335 nm (4 200); $\nu_{max.}$ 1 670 cm^{-1} (C=O); τ 2.2—3.6 (16 H, m, arom. H) and 7.75 (3 H, s, Me); *m/e* 337 ($M^{+\cdot}$); 1-p-*chlorophenyl*-4,6-*diphenyl*-2-*pyridone* (10d) (60%), prisms, m.p. 208—210 °C (Found: C, 77.3; H, 4.7; Cl, 9.8; N, 4.0. $C_{23}H_{16}ClNO$ requires C, 77.2; H, 4.5; Cl, 9.9; N, 3.9%); $\lambda_{max.}$ 225 (ε 13 000), 250 (13 000), and 335 nm (5 000); $\nu_{max.}$ 1 670 cm^{-1} (C=O); τ 2.0—3.5 (m, arom. H); *m/e* 357 ($M^{+\cdot}$); 4,6-*diphenyl*-1-(2-*pyridyl*)-2-*pyridone* (10e) (60%), prisms, m.p. 200—202 °C (Found: C, 81.4; H, 5.0; N, 8.6. $C_{22}H_{16}N_2O$ requires C, 81.5; H, 4.9; N, 8.4%); $\lambda_{max.}$ 220 (ε 9 000), 225 (11 000), and 335 nm (4 400); $\nu_{max.}$ 1 660 cm^{-1} (C=O); τ 1.5—3.5 (m, arom. H); *m/e* 324 ($M^{+\cdot}$); 1-(5-*methyl*-2-*pyridyl*)-4,6-*diphenyl*-2-*pyridone* (10f) (70%), needles, m.p. 217—220 °C (Found: C, 81.8; H, 5.4, N, 8.0. $C_{23}H_{18}N_2O$ requires C, 81.7; H, 5.3; N, 8.3%); $\lambda_{max.}$ 220 (ε 9 000), 250 (14 000), and 335 nm (4 000); $\nu_{max.}$ 1 660 cm^{-1} (C=O); τ 1.7—3.6 (15 H, m, arom. H) and 7.80 (3 H, s, Me); *m/e* 338 ($M^{+\cdot}$); 1-(4-*methyl*-2-*pyridyl*)-4,6-*diphenyl*-2-*pyridone* (10g) (60%), prisms, m.p. 160—162 °C (Found: C, 81.3; H, 5.3; N, 8.5%); $\lambda_{max.}$ 220 (ε 9 200), 250 (15 000), and 330 nm (3 600); $\nu_{max.}$ 1 665 cm^{-1} (C=O); τ 1.7—3.6 (15 H, m, arom. H) and 7.80 (3 H, s, Me); *m/e* 338 ($M^{+\cdot}$); 1-(3-*methyl*-2-*pyridyl*)-4,6-*diphenyl*-2-*pyridone* (10h) (40%), prisms, m.p. 204—206 °C (Found: C, 81.5; H, 5.5; N, 8.2%); $\lambda_{max.}$ 222 (ε 10 800), 252 (12 800), and 335 nm (4 600); $\nu_{max.}$ 1 655 cm^{-1} (C=O); τ 1.6—3.6 (15 H, m, arom. H) and 7.80 (3 H, s, Me); *m/e* 338 ($M^{+\cdot}$).

Rearrangement of 4,6,N-*Triphenylpyran*-2-*imine* (9a).—Sodium (0.3 g) was dissolved in EtOH (20 ml) and compound (9a) (1.4 g) was added to the solution, which was then heated under reflux (8 h). After cooling, the solution was added to water (50 ml) and the solid which separated was collected and recrystallised from EtOH to give 1,4,6-triphenyl-2-pyridone (10a) (0.9 g, 60%), prisms, m.p. 164—166 °C, identical with that of an authentic sample.

Preparation of 2-*Amino*-4,6-*diphenylthiopyrylium Iodides* (19).—(i) *From primary aromatic amines.* 2-Methylthio-4,6-diphenylthiopyrylium iodide (18) (0.42 g) and aniline (0.1 g) were fused at 70—80 °C. EtOH (20 ml) was then added and the solution heated at reflux temperature (8 h). Evaporation and recrystallisation from EtOH gave 2-*anilino*-4,6-*diphenylthiopyrylium iodide* (19a) (0.33 g, 70%) as red prisms, m.p. 170—172 °C (Found: C, 59.4; H, 4.2; N, 3.2. $C_{23}H_{18}INS$ requires C, 59.1; H, 3.9; N, 3.0%); $\lambda_{max.}$ 225 (ε 12 000), 275 (10 800), and 390 nm (3 000); $\nu_{max.}$ 1 620 cm^{-1} (C=N); τ 1.5br (s, NH) and 2.2—3.0 (m, arom. H); *m/e* 339 ($M^{+\cdot}$ — HI).

The following iodides were similarly prepared from the appropriate arylamines: 4,6-*diphenyl*-2-(o-*toluidino*)*thiopyrylium iodide* (19b) (61%), red prisms, m.p. 200 °C (decomp.) (Found: C, 60.1; H, 4.4; N, 2.7. $C_{24}H_{20}INS$ requires C, 59.9; H, 4.2; N, 2.9%); $\lambda_{max.}$ 225 (ε 11 000), 275 (13 000), and 400 nm (2 800); $\nu_{max.}$ 1 625 cm^{-1} (C=N); τ 2.2—3.3 (17 H, m, arom. H + NH) and 7.78 (3 H, s, Me); *m/e* 353 ($M^{+\cdot}$ — HI); 4,6-*diphenyl*-2-(p-*toluidino*)-*thiopyrylium iodide* (19c) (70%), red prisms, m.p. 220—222 °C (Found: C, 59.8; H, 4.2; N, 3.0. $C_{24}H_{20}INS$ requires C, 59.9; H, 4.2; N, 2.9%); $\lambda_{max.}$ 225 (ε 12 000), 275 (10 800), and 390 nm (2 800); $\nu_{max.}$ 1 620 cm^{-1} (C=N); τ 1.1br (s, NH), 2.0—3.0 (16 H, m, arom. H), and 7.62 (3 H, s, Me); *m/e* 353 ($M^{+\cdot}$ — HI); 2-(m-*nitroanilino*)-4,6-*diphenylthiopyrylium iodide* (19d) (50%), yellow prisms, m.p. 208—212 °C (Found: C, 54.3; H, 3.7; N, 5.2. $C_{23}H_{17}IN_2O_2S$ requires C, 53.9; H, 3.3; N, 5.5%); $\lambda_{max.}$ 220 (ε 4 600), 276 (10 400), and 390 nm (2 400); $\nu_{max.}$ 1 610 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 0.9—2.3 (m, arom. H); *m/e* 384 ($M^{+\cdot}$ — HI); 4,6-*diphenyl*-2-(2-*pyridylamino*)*thiopyrylium iodide* (19e) (50%), brown needles, m.p. 207—210 °C (decomp.) (Found: C, 56.1; H, 3.6; N, 5.7; S, 6.9. $C_{22}H_{17}IN_2S$ requires C, 56.4; H, 3.6; N, 6.0%); $\lambda_{max.}$ 300 (ε 11 000), 330sh (5 000), and 410 nm (6 800) nm; $\nu_{max.}$ 3 400 (NH) and 1 610 cm^{-1} (C=N); τ 0.45 (s, NH) and 1.0—2.5 (m, arom. H); *m/e* 340 ($M^{+\cdot}$ — HI); 2-(5-*methyl*-2-*pyridylamino*)-4,6-*diphenylthiopyrylium iodide* (19f) (60%), brown needles, m.p. 232—234 °C (Found: C, 57.6; H, 4.1; N, 5.9. $C_{23}H_{19}IN_2S$ requires C, 57.3; H, 3.9; N, 5.8%); $\lambda_{max.}$ 225 (ε 13 000), 240sh (8 400), 300 (11 000), 340sh (5 000), and 430 nm (5 000); $\nu_{max.}$ 1 620 cm^{-1} (C=N); τ 0.7 (s, NH), 1.6—2.8 (15 H, m, arom. H), and 7.65 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$ — HI); 2-(4-*methyl*-2-*pyridylamino*)-4,6-*diphenylthiopyrylium iodide* (19g) (60%), red needles, m.p. 244—246 °C (Found: C, 57.2; H, 4.4; N, 5.7%); $\lambda_{max.}$ 225 (ε 9 000), 288 (7 200), and 430 nm (3 800); $\nu_{max.}$ 1 610 cm^{-1} (C=N); τ 0.60 (s, NH), 1.5—3.1 (15 H, m, arom. H), and 7.60 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$ — HI); 2-(3-*methyl*-2-*pyridylamino*)-4,6-*diphenylthiopyrylium iodide* (19h) (60%), yellow needles, m.p. 200 °C (decomp.) (Found: C, 57.2; H, 4.2; N, 6.0%); $\lambda_{max.}$ 225 (ε 8 000), 282 (11 800), and 415 nm (3 000); $\nu_{max.}$ 1 610 cm^{-1} (C=N); τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 1.2—3.0 (15 H, m, arom. H) and 7.45 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$ — HI).

(ii) *From secondary amines*. Using the procedure described above the following iodides were prepared from the appropriate secondary amines: *2-dimethylamino-4,6-diphenylthiopyrylium iodide* (20i) (60%), yellow needles, m.p. 250 °C (decomp.) (Found: C, 54.2; H, 4.4; N, 3.3. $C_{19}H_{18}INS$ requires C, 54.5; H, 4.3; N, 3.3%); $\lambda_{max.}$ 225 (ε 11 200), 282 (6 200), 332 (6 000), and 410 nm (4 400); $\nu_{max.}$ 1 605 cm^{-1} (C=N + C=C); τ ($CF_3{\cdot}CO_2H$) 2.0—2.6 (12 H, m, arom. H) and 6.31 (6 H, s, NMe); *2-(N-methylanilino)-4,6-diphenylthiopyrylium iodide* (20j) (70%), yellow needles, m.p. 243—245 °C (Found: C, 59.6; H, 4.5; N, 3.2. $C_{24}H_{20}INS$ requires C, 59.9; H, 4.2; N, 2.9%); $\lambda_{max.}$ 225 (ε 9 200), 280 (600), 325 (4 800), and 400 nm (3 200); $\nu_{max.}$ 1 600 cm^{-1} (C=N + C=C); τ ($CF_3{\cdot}CO_2H$) 2.0—2.7 (17 H, m, arom. H) and 6.06 (3 H, s, NMe); *4,6-diphenyl-2-pyrrolidin-1-ylthiopyrylium iodide* (20k) (70%), yellow needles, m.p. 274—276 °C (Found: C, 56.3; H, 4.8; N, 2.9. $C_{21}H_{20}INS$ requires C, 56.6; H, 4.5; N, 3.1%); $\lambda_{max.}$ 225 (ε 12 000), 285 (8 000), 325 (5 200), and 405 nm (3 800); $\nu_{max.}$ 1 610 cm^{-1} (C=N + C=C); τ ($CF_3{\cdot}CO_2H$) 2.0—2.7 (12 H, m, arom. H), 6.10 (4 H, m, NCH_2), and 7.60 (4 H, m, $CH_2{\cdot}CH_2$); *4,6-diphenyl-2-piperidinothiopyrylium iodide* (20l) (70%), yellow needles, m.p. 266—269 °C (Found: C, 57.3; H, 5.1; N, 2.7. $C_{22}H_{22}INS$ requires C, 57.5; H, 4.8; N, 3.0%); $\lambda_{max.}$ 225 (ε 9 000), 285 (6 800), 330 (4 000), and 415 nm (3 000); $\nu_{max.}$ 1 600 (C=N + C=C) cm^{-1}; τ ($CF_3{\cdot}CO_2H$) 1.9—2.6 (12 H, m, arom. H), 5.90 (4 H, m, NCH_2), and 8.00 (6 H, m, $CH_2{\cdot}CH_2$); *2-morpholino-4,6-diphenylthiopyrylium iodide* (20m) (62%), yellow needles, m.p. 280—282 °C (Found: C, 54.4; H, 4.5; N, 3.3. $C_{21}H_{20}INOS$ requires C, 54.7; H, 4.3; N, 3.0%); $\lambda_{max.}$ 225 (ε 11 000), 285 (7 500), 320 (5 500), and 410 nm (3 200); $\nu_{max.}$ 1 600 cm^{-1} (C=N + C=C); τ ($CF_3{\cdot}CO_2H$) 1.9—2.6 (12 H, m, arom. H) and 5.74 (8 H, m, CH_2).

Preparation of 4,6-Diphenylthiopyran-2-imines (21).—*4,6-Diphenyl-N-o-tolylthiopyran-2-imine* (21b). Compound (19b) (0.001 mol, 0.5 g) and NaOEt (0.34 g) in EtOH (20 ml) were heated under reflux (6 h) and cooled to give a solid which was recrystallised from EtOH to give compound (21b) (60%), red needles, m.p. 179—181 °C (Found: C, 81.3; H, 5.3; N, 3.7. $C_{24}H_{19}NS$ requires C, 81.6; H, 5.4; N, 4.0%); $\lambda_{max.}$ 228 (ε 11 000), 275 (13 000), and 390 nm (3 800); $\nu_{max.}$ 1 622 cm^{-1} (C=N); τ 2.2—3.3 (16 H, m, arom. H) and 7.79 (3 H, s, Me); *m/e* 353 ($M^{+\cdot}$).

The following derivatives were similarly obtained: *4,6-diphenyl-N-p-tolylthiopyran-2-imine* (21c) (70%), red needles, m.p. 110—112 °C (Found: C, 81.3; H, 5.5; N, 3.9; S, 9.1. $C_{24}H_{19}NS$ requires C, 81.6; H, 5.4; N, 4.0; S, 9.1%); $\lambda_{max.}$ 225 (ε 10 800), 275 (12 800), and 400 nm (2 200); $\nu_{max.}$ 1 620 cm^{-1} (C=N); τ 2.3—3.3 (16 H, m, arom. H) and 7.66 (3 H, s, Me); *m/e* 353 ($M^{+\cdot}$); *N-(5-methylpyridyl)-4,6-diphenylthiopyran-2-imine* (21f) (70%), yellow fibrous needles, m.p. 76—78 °C (Found: C, 78.0; H, 5.3; N, 7.9; S, 9.0. $C_{23}H_{18}N_2S$ requires C, 78.0; H, 5.1; N, 7.9; S, 9.0%); $\lambda_{max.}$ 230 (ε 8 200), 285 (12 000), and 425 nm (5 000); $\nu_{max.}$ 1 600 and 1 620 cm^{-1} (C=C + C=N); τ 1.65 (1 H, s, arom. CH), 2.2—3.0 (14 H, m, arom. H), and 7.70 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$); *N-(4-methyl-2-pyridyl)-4,6-diphenylthiopyran-2-imine* (21g) (50%), yellow needles, m.p. 110—120 °C (decomp.) (Found: C, 77.6; H, 5.1; N, 7.6%); $\lambda_{max.}$ 225 (ε 7 800), 282 (9 200), and 420 nm (3 000); $\nu_{max.}$ 1 615 cm^{-1} (C=N); τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 1.7—3.6 (15 H, m, arom. H) and 7.75 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$); *2-(3-methyl-2-pyridyl)-4,6-diphenylthiopyran-2-imine* (21h) (40%), yellow needles, m.p. 105—107 °C (Found: C, 77.7; H, 5.2; N, 7.7; S, 8.9%); $\lambda_{max.}$ 220 (ε 7 000), 282 (8 400), and 415 nm (1 800); $\nu_{max.}$ 1 615 cm^{-1} (C=N); τ 1.1—2.5 (15 H, m, arom. H) and 7.30 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$).

N-(1,2-Dihydro-2-oxo-1-pyridyl)-4,6-diphenylthiopyran-2-imine (21n).—Compound (18) (0.42 g, 0.001 mol) and *N*-amino-2-pyridone (0.11 g, 0.001 mol) were treated as described in the preparation of (19a). The crude iodide was not characterised but repeated recrystallisation from EtOH gave the free imine, *compound* (21n) (0.22 g, 60%), yellow prisms, m.p. 198—200 °C (Found: C, 74.3; H, 4.7; N, 8.2. $C_{22}H_{16}N_2OS$ requires C, 74.2; H, 4.5; N, 7.9%); $\lambda_{max.}$ 225 (ε 8 800), 275 (9 200), and 380 nm (2 800); $\nu_{max.}$ 1 655 cm^{-1} (C=O); τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 1.6—3.5 (m, arom. H); *m/e* 356 ($M^{+\cdot}$).

Similarly prepared was *4,6-diphenyl-N-(1,2,4-triazol-4-yl)-thiopyran-2-imine* (21o) (55%), yellow needles, m.p. 237—238 °C (Found: C, 68.8; H, 4.3; N, 16.8; S, 9.6. $C_{19}H_{14}N_4S$ requires C, 69.1; H, 4.2; N, 17.0; S, 9.7%); $\lambda_{max.}$ 280 (ε 13 200), and 375 nm (5 200); $\nu_{max.}$ 1 610 cm^{-1} (C=N); τ 1.8br (2 H, s, triazolyl H) and 2.1—3.1 (10 H, m, arom. H); *m/e* 330 ($M^{+\cdot}$); *N-benzamido-4,6-diphenylthiopyran-2-imine* (21p) (41%), orange prisms, m.p. 172—174 °C (Found: C, 75.0; H, 5.0; N, 7.2; S, 8.1. $C_{24}H_{18}N_2OS$ requires C, 75.4; H, 4.7; N, 7.3; S, 8.4%); $\lambda_{max.}$ 282 (ε 11 240) and 400 nm (3 400); $\nu_{max.}$ 1 640 (C=O) and 1 605 cm^{-1} (C=N); τ 1.7—2.7 (17 H, m, arom. H); *m/e* 382 ($M^{+\cdot}$).

Reaction of 2-Methylthio-4,6-diphenylthiopyrylium Iodide (18) *with Phenylenediamines*.—(a) *With* p-*phenylenediamine*. The iodide (18) (0.84 g) and *p*-phenylenediamine (0.11 g) in EtOH (20 ml) were heated under reflux (8 h) and cooled to give a solid which was collected and washed with hot EtOH to yield *4,4′,6,6′-tetraphenyl-NN′-p-phenylenebis(thiopyran-2-imine)* (22a) (0.24 g, 40%), red prisms, m.p. 261—263 °C (Found: C, 79.9; H, 4.7; N, 4.4; S, 10.4. $C_{40}H_{28}N_2S_2$ requires C, 80.0; H, 4.7; N, 4.7; S, 10.7%); $\lambda_{max.}$ 225 (ε 9 200), 282 (11 000), and 405 nm (2 000); $\nu_{max.}$ 1 600 cm^{-1} (C=N + C=C); τ [$(CD_3)_2SO$] 1.5—2.5 (m, arom. H).

(b) *With* m-*phenylenediamine*. A procedure as in (a) gave *4,4′,6,6′-tetraphenyl-NN′-m-phenylenebis(thiopyran-2-imine)* (32b) (30%) as red needles, m.p. 176—178 °C (Found: C, 79.8; H, 4.9; N, 4.9; S, 10.6. $C_{40}H_{28}N_2S_2$ requires C, 80.0; H, 4.7; N, 4.7; S, 10.7%); $\lambda_{max.}$ 225 (ε 9 500), 282 (11 200), and 415 nm (2 000); $\nu_{max.}$ 1 625 cm^{-1} (C=N); τ 2.2—3.4 (m, arom. H).

(c) *With* o-*phenylenediamine*. Compound (18) (0.42 g) and *o*-phenylenediamine (0.11 g) in EtOH (20 ml) were heated under reflux (4 h) and cooled; the solid product was recrystallised from EtOH giving *1,3-diphenylpyrido*[1,2-a]*benzimidazole* (23) (0.2 g, 62%), brown needles, m.p. 161—163 °C (Found: C, 86.2; H, 4.8; N, 8.8. $C_{23}H_{16}N_2$ requires C, 86.3; H, 5.0; N, 8.8%); $\lambda_{max.}$ 217 (ε 5 600), 270 (11 400), 315 (4 000), and 355 nm (3 500); $\nu_{max.}$ 1 645 cm^{-1} (C=N); τ ($CDCl_3$–$CF_3{\cdot}CO_2H$) 1.6—3.6 (m, arom. H). Compound (23) (0.32 g) was stirred at room temperature (10 h) with MeI (5 ml). Evaporation of the excess of MeI and recrystallisation from EtOH gave *N-methyl-1,3-diphenylpyrido*[1,2-a]*benzimidazolium iodide* (24) (0.33 g, 70%), brown prisms, m.p. 280—282 °C (Found: C, 62.2; H, 4.2; N, 6.2. $C_{24}H_{19}IN_2$ requires C, 62.3; H, 4.1; N, 6.1%); $\lambda_{max.}$ 225 (ε 11 000), 272 (9 000), 317 (7 000), and 355 nm (5 000); $\nu_{max.}$ 1 645 cm^{-1} (C=N); τ ($CF_3{\cdot}CO_2H$) 1.7—3.3 (m, arom. H) and 5.65 (s, NMe); *m/e* 320 ($M^{+\cdot}$ — MeI).

Preparation of 1-Aryl-4,6-diphenylpyridine-2-thiones (25).—4,6-Diphenyl-1-(*p*-tolyl)-2-pyridone (10c) (1.1 g) and P_4S_{10} (2.2 g) in pyridine (30 ml) were heated under reflux (12 h). The cooled mixture was thrown into water (100 ml) with

stirring (1 h). The solid product was collected, dried, and extracted with $CHCl_3$. The extract was evaporated; recrystallisation of the residue from EtOH–Et_2O gave *4,6-diphenyl-1-(p-tolyl)pyridine-2-thione* (25e) (0.9 g, 60%), yellow prisms, m.p. 229—231 °C (Found: C, 81.4; H, 5.3; N, 4.4; S, 9.2. $C_{24}H_{19}NS$ requires C, 81.6; H, 5.4; N, 4.0; S, 9.1%); $\lambda_{max.}$ 220 (ε 10 200), 280 (12 000), and 375 nm (3 800); $\nu_{max.}$ 1 620 (C=N) and 1 165 cm^{-1} (C=S); τ 1.9—3.2 (16 H, m, arom. H) and 7.76 (3 H, s, Me); *m/e* 353 ($M^{+\cdot}$). Concentration of the mother liquor gave more crystals, identified as 4,6-diphenylpyridine-2-thione (28) (10%), yellow prisms, m.p. 190—192 °C (lit.,[11] 197 °C) (Found: N, 5.5. Calc. for $C_{17}H_{13}NS$: N, 5.3%); $\lambda_{max.}$ 210 (ε 11 000), 255 (12 200), and 400 nm (1 800); $\nu_{max.}$ 1 140 cm^{-1} (C=S); τ 2.0—3.0 (arom. H + NH). Further concentration of the mother liquor gave, after several days, bis-(4,6-diphenyl-2-pyridyl) disulphide (29) (10%), prisms, m.p. 200—205 °C (lit.,[11] m.p. 205 °C) (Found: C, 77.6; H, 4.7; N, 5.3; S, 12.1. Calc. for $C_{34}H_{24}N_2S_2$: C, 77.9; H, 4.6; N, 5.3; S, 12.2%); $\lambda_{max.}$ 220 (ε 6 600), 255 (12 600), and 315 nm (3 000); $\nu_{max.}$ 1 590 cm^{-1} (C=N); τ 1.8—2.6 (m, arom. H).

In a similar manner the following derivatives were prepared: *4,6-diphenyl-1-(o-pyridyl)pyridine-2-thione* (25a) (50%), yellow prisms, m.p. 154—156 °C (Found: C, 77.4; H, 4.9; N, 8.2; S, 9.4. $C_{22}H_{16}N_2S$ requires C, 77.6; H, 4.7; N, 8.2; S, 9.4%); $\lambda_{max.}$ 217 (ε 8 000), 282 (12 000), and 400 nm (3 200); $\nu_{max.}$ 1 620 (C=N) and 1 170 cm^{-1} (C=S); τ 1.2—3.1 (m, arom. H); *m/e* 340 ($M^{+\cdot}$) [together with compound (28) (20%) and compound (29) (25%)]; *1-(5-methyl-2-pyridyl)-4,6-diphenylpyridine-2-thione* (25b) (60%), yellow prisms, m.p. 170 °C (decomp.) (Found: C, 78.2; H, 5.4; N, 7.6; S, 9.0. $C_{23}H_{18}N_2S$ requires C, 78.0; H, 5.1; N, 7.9; S, 9.0%); $\lambda_{max.}$ 220 (ε 7 000), 280 (11 800), and 400 nm (2 400); $\nu_{max.}$ 1 620 (C=N) and 1 170 cm^{-1} (C=S); τ 1.7—3.2 (15 H, m, arom. H) and 7.77 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$); together with compound (28) (10%) and compound (29) (10%) [the liquors from this experiment yielded a fourth product, 4,6-diphenylpyridyl 5-methylpyridylsulphide (27b) (5%), m.p. 86—88 °C, identical with an authentic sample described below].

Attempted Preparation of 1-(4-Methyl-2-pyridyl)-4,6-diphenylpyridine-2-thione (25c).—1-(4-Methyl-2-pyridyl)-4,6-diphenyl-2-pyridone (10 g) (0.01 mol, 2.4 g) and P_4S_{10} (0.03 mol, 6.6 g) in pyridine (20 ml) were heated under reflux (8 h). The solvent was distilled off and the residue was extracted with $CHCl_3$. Evaporation of the solvent and recrystallisation of the residue from EtOH–Et_2O (50%) gave *2-(4-methyl-2-pyridylthio)-4,6-diphenylpyridine* (27c) (0.7 g, 20%) as prisms, m.p. 94—96 °C (Found: C, 77.8; H, 5.2; N, 7.9; S, 9.2. $C_{23}H_{18}N_2S$ requires C, 78.0; H, 5.1; N, 7.9; S, 9.0%); $\lambda_{max.}$ 220 (ε 7 400), 252 (14 200), and 320 nm (3 000); $\nu_{max.}$ 1 590 cm^{-1} (C=N); τ 1.5—3.0 (15 H, m, arom. H) and 7.6 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$). Concentration of the filtrate gave more crystals identified as compound (28) (20%), identical with an authentic sample. A third crop of crystals, which separated from the filtrate was identified as compound (29) (20%), identical with an authentic sample.

In a similar experiment compound (10h) (0.01 mol; 2.4 g) with phosphorus pentasulphide (0.03 mol, 6.6 g) gave only compounds (28) (30%) and (29) (20%).

Bis-(4,6-diphenylpyridyl) Disulphide (29).—4,6-Diphenylpyridine-2-thione (28) (0.26 g) in EtOH (10 ml) was added to a solution of $FeCl_3$ (0.16 g) in water (5 ml) and the mixture was stirred (1 h). The solution was diluted (H_2O) and extracted with $CHCl_3$. Evaporation of the $CHCl_3$ and recrystallisation of the residue from Et_2O gave compound (29) (0.13 g, 25%), m.p. 200—205 °C, identical with a sample prepared as above.

Thermolysis of 1-(5-Methyl-2-pyridyl)-4,6-diphenylpyridine-2-thione (25b).—Compound (25b) (0.8 g) was heated at 210—230 °C (10 min). After cooling, EtOH (2 ml) and light petroleum (b.p. 40—60 °C) (20 ml) were added; the mixture was left overnight and gave *4,6-diphenyl-2-pyridyl 5-methyl-2-pyridyl sulphide* (27b) (0.32 g, 40%), light yellow prisms, m.p. 86—88 °C (Found: C, 77.9; H, 5.2; N, 8.1; S, 9.0. $C_{23}H_{18}N_2S$ requires C, 78.0; H, 5.1; N, 7.9; S, 9.0%); $\lambda_{max.}$ 220 (ε 7 400), 255 (12 400), and 325 nm (3 000); $\nu_{max.}$ 1 590 cm^{-1} (C=N + C=C); τ 1.5—3.0 (15 H, m, arom. H) and 7.75 (3 H, s, Me); *m/e* 354 ($M^{+\cdot}$).

Methylation of 1-Aryl-4,6-diphenylpyridine-2-thiones (25). —4,6-Diphenyl-1-(*p*-tolyl)pyridine-2-thione (25e) (0.35 g, 0.001 mol) and MeI (5 ml) in $CHCl_3$ solution (5 ml) were stirred (12 h) at room temp. Evaporation and recrystallisation of the residue from EtOH–light petroleum (b.p 40—60 °C) gave *2-methylthio-4,6-diphenyl-1-(p-tolyl)pyridinium iodide* (26e) (0.3 g, 60%), yellow prisms, m.p. 215—217 °C (Found: C, 60.5; H, 4.5; I, 25.3; N, 3.1; S, 6.6. $C_{25}H_{22}INS$ requires C, 60.6; H, 4.4; I, 25.7; N, 2.8; S, 6.5%); $\lambda_{max.}$ 220 (ε 12 800), 262 (8 200), 300 (10 000), and 350 nm (5 800); $\nu_{max.}$ 1 615 cm^{-1} (C=N); τ 1.7—3.1 (16 H, m, arom. H), 7.10 (3 H, s, SMe), and 7.65 (3 H, s, CMe); *m/e* 368 ($M^{+\cdot}$ − I).

The following iodides were similarly prepared: *2-methylthio-4,6-diphenyl-1-(2-pyridyl)pyridinium iodide* (26a) (65%), yellow prisms, m.p. 210—212 °C (decomp.) (Found: C, 56.9; H, 4.2; I, 26.5; N, 5.8; S, 6.5. $C_{23}H_{19}IN_2S$ requires C, 57.3; H, 3.9; I, 26.4; N, 5.8; S, 6.6%); $\lambda_{max.}$ 220 (ε 12 000), 262 (7 000), 310 (11 000), and 352 nm (5 600); $\nu_{max.}$ 1 615 cm^{-1} (C=N); τ 1.4—2.9 (16 H, m, arom. H) and 7.12 (3 H, s, SMe); *m/e* 355 ($M^{+\cdot}$); *2-methylthio-1-(5-methyl-2-pyridyl)-4,6-diphenylpyridinium iodide* (26b) (70%), yellow prisms, m.p. 195—197 °C (Found: C, 58.3; H, 4.3; N, 5.7. $C_{24}H_{21}IN_2S$ requires C, 58.1; H, 4.2; N, 5.6%); $\lambda_{max.}$ 220 (ε 11 000), 262 (6 600), 310 (10 000), and 350 nm (5 000); $\nu_{max.}$ 1 620 cm^{-1} (C=N); τ 1.6—2.8 (15 H, m, arom. H), 7.08 (3 H, s, SMe), and 7.62 (3 H, s, CMe); *m/e* 369 ($M^{+\cdot}$ − I).

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