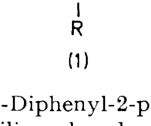
The 2-Pyridone–Pyran-2-imine and Pyridine-2-thione–Thiopyran-2-imine Systems; Interconversions and Characterisation of Isomeric Species

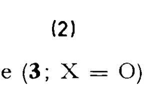
By A. Sultan Afridi, Alan R. Katritzky,* and Christopher A. Ramsden
(*School of Chemical Sciences, University of East Anglia, Norwich* NR4 7TJ)

Summary Whereas 2-arylamino-4,6-diphenylpyrylium chlorides are readily converted into 2-pyridones, the corresponding 2-arylamino-4,6-diphenylthiopyrylium iodides do not give pyridine-2-thiones; mass spectra unambiguously distinguish between isomeric structures in these series.

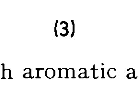
Although examples of the isomeric species (**1**) and (**2**) have been prepared for both $X = O$ and $X = S$, [1–3] unambiguous support for their structural assignments (**1**) or (**2**) has in neither case been provided. Thus pairs of isomeric derivatives (**1**) and (**2**) have not been compared directly nor has the interconversion of isomers (**1**) $\rightleftharpoons$ (**2**) been observed. We now report studies which firmly establish the interrelationship of these structural types (**1** and **2**; $X = O$ or S).



(1)



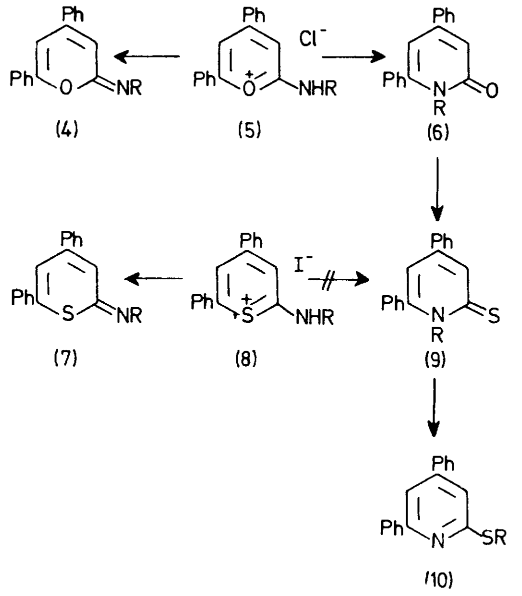
(2)



(3)

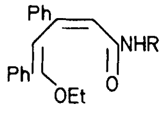
4,6-Diphenyl-2-pyrone (**3**; $X = O$) with aromatic amines in boiling phosphoryl chloride[2] gives the yellow, crystalline pyrylium chlorides (**5a**—**h**). These salts (**5**) can be deprotonated (pyridine–MeOH) giving the pyranimines (**4**) but treatment of the salts (**5**) with sodium ethoxide in hot ethanol results in a novel rearrangement to the isomeric pyridones (**6a**—**h**). The primary product in this base-catalysed reaction (**5**) → (**6**) is probably the free pyranimine (**4**); in this connection we have demonstrated that the rearrangement (**4a**) → (**6a**) takes place in 60% yield in ethanolic sodium ethoxide solution. This transformation (**4**) → (**6**) is analogous to rearrangements of isoelectronic meso-ionic systems[4] and may well proceed *via* the acyclic intermediate (**11**). The isomeric species (**4**) and (**6**) have similar physical and spectroscopic properties [(**4a**), m.p. 160 °C, λ_{max} (EtOH) 215 (ϵ 6200), 275 (13,200), and 395 nm (4000); ν_{max} (Nujol) 1655 cm^{-1}; (**6a**), m.p. 164—166 °C; λ_{max} (EtOH) 220 (ϵ 11,400), 250 (13,400), and 337 nm (4800); ν_{max} (Nujol) 1675 cm^{-1}] but are readily distinguished by mass spectrometry. Both isomers show a molecular ion ($M^{\cdot+}$) but the fragmentations (**4**; $M^{\cdot+} \rightarrow$ Ph-C≡O^+) and [**6**; $M^{\cdot+} \rightarrow (M^{\cdot+} - CO)$] are discriminating.

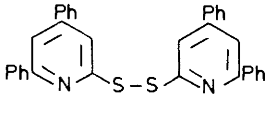
Treatment of the pyridones (**6**) with P_4S_{10}-pyridine gives products whose structures are governed by the nitrogen substituent (R). The *p*-tolyl derivative (**6c**; R = *p*-Me·C_6H_4) gives the pyridinthione (**9c**) (60%), m.p. 229—231 °C, together with low yields of the unsubstituted pyridinthione (**9**; R = H) (5%) and its oxidation product (**12**) (5%), and similar results were obtained using the pyridones (**6e**, **f**). Compound (**6f**) also gave a low yield (5%) of the sulphide (**10f**), m.p. 77 °C. This product (**10f**) is formed by a Chapman rearrangement of the pyridinthione (**9f**); in a separate experiment thermolysis of (**9f**) (210—230 °C; 10 min) gave (**10f**) (40%). Attempts to prepare the pyridinthiones (**9g**,**h**) were not successful. High yields of the by-products (**9**; R = H) and (**12**) (20—30%) were obtained although the pyridone (**6g**) did give the Chapman rearrangement product (**10g**), m.p. 90 °C, in 20% yield.



a; R = Ph
b; R = o-MeC$_6$H$_4$
c; R = p-MeC$_6$H$_4$
d; R = p-ClC$_6$H$_4$
e; R = 2-pyridyl
f; R = 5-methyl-2-pyridyl
g; R = 4-methyl-2-pyridyl
h; R = 3-methyl-2-pyridyl

The reaction of the methiodides of 4,6-diphenylthiopyran-2-thione (**3**; X = S) with aromatic amines[3] gives the orange, crystalline thiopyrylium iodides (**8b**,**c**, **f**—**h**) which we have converted into the free imines (**7b**,**c**, **f**—**h**) by deprotonation using sodium ethoxide in ethanolic solution. In contrast to the behaviour of pyrylium chlorides, (**5**) → (**6**), the thiopyrylium iodides (**8**) are not rearranged to the pyridinthiones (**9**) under these conditions. The isomeric systems (**7**) and (**9**) have similar spectral properties [(**7c**), m.p. 110—112 °C; $\lambda_{\max}$ (EtOH) 225 (ϵ 10,800), 275 (12,800), and 400 nm (2200); $\nu_{\max}$ (Nujol) 1620 cm^{-1}: (**9c**), m.p. 229—231 °C; $\lambda_{\max}$ (EtOH) 220 (ϵ 10,200), 280 (12,000), and 375 nm (3800); $\nu_{\max}$ (Nujol) 1620 cm^{-1}] but are again readily distinguished on the basis of their mass spectral fragmentation patterns. Both species give molecular ions ($M^{\cdot+}$) but the thiopyranimines (**7**) are unambiguously characterised by the observation of the fragment ion $\mathrm{Ph{-}C{\equiv}S^+}$ (*m*/*e* 121).


(11)


(12)

Since the structures of the isomeric species (**4**) and (**6**), and (**7**) and (**9**), and the salts (**5**) and (**8**) have now been unambiguously established by chemical methods, the recognition of their characteristic mass spectral fragmentation patterns should provide a useful method for discrimination in future studies on these structural types.

(*Received*, 12*th July* 1976; *Com.* 795.)

---

[1] I. E.-S. El-Kholy, F. K. Rafla, and M. M. Mishrikey, *J. Chem. Soc.* (*C*), 1970, 1578; H. Behringer and A. Grimm, *Annalen*, 1965, **682**, 188.

[2] J. A. Van Allan and S. C. Chang, *J. Heterocyclic Chem.*, 1974, **11**, 1065.

[3] J. Faust, G. Speier, and R. Mayer, *J. prakt. Chem.*, 1969, **311**, 61.

[4] W. D. Ollis and C. A. Ramsden, *Adv. Heterocyclic Chem.*, 1976, **19**, 1; A. R. McCarthy, W. D. Ollis, and C. A. Ramsden, *J.C.S. Perkin I*, 1974, 627; W. D. Ollis and C. A. Ramsden, *ibid.*, 1974, **633**, **638**; R. N. Hanley, W. D. Ollis, and C. A. Ramsden, *J.C.S. Chem. Comm.*, 1976, **306**; E. Cawkill, W. D. Ollis, C. A. Ramsden and G. P. Rowson, *ibid.*, p. **439**.