The Preparation and Solvatochromic Properties of Vinylogous α-Pyridones

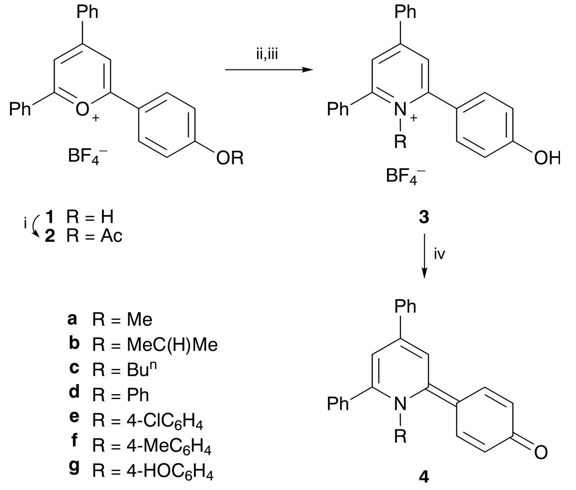
J. Chem. Research (S),
1998, 106–107
J. Chem. Research (M),
1998, 0601–0613

Juan Soto Galdames and Marcos Caroli Rezende[*]

Facultad de Quimica y Biologia, Universidad de Santiago de Chile, Casilla 40, Santiago, Correo 33, Chile

The preparation and the solvatochromic properties of the dyes **4** are described.

As part of our interest in the solvatochromic properties of pyridiniophenolates[1–4] we synthesised a series of vinylogous α-pyridones **4** by *in situ* treatment of the corresponding *N*-substituted pyridinium fluoroborate **3** with sodium hydroxide. The latter salts were synthesized from the 2,4-diphenyl-6-(4-hydroxyphenyl)pyrylium fluoroborate **1**[4] or its acetylated derivative **2**.

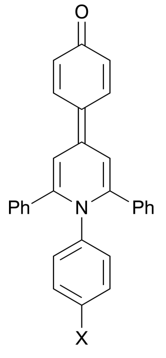


Scheme 1 *Reagents*: i, Ac_2O; ii, RNH_2–Et_3N; iii, HBF_4–H_2O; iv, OH^-

The position of the longest-wavelength charge transfer band for all dyes **4**, recorded in a variety of solvents, is given in Table 1. Compounds **4** exhibited a negative solvatochromic behaviour in polar solvents, reversing this trend in low polarity media ($E_T^N < 0.4$). This reversed behaviour was in agreement with semi-empirical calculations utilizing the AM1 hamiltonian and a simple model where a $+2$ charge positioned along the C═O bond at a variable distance from the oxygen atom was employed to mimic environmental polarity variations.[3,4]

Although it is difficult to draw a clear-cut distinction between the *N*-alkyl and the *N*-aryl substituted dyes, inspection of Table 1 reveals a tendency of the latter to absorb at higher wavelengths in more polar media than their respective *N*-alkyl analogues.

For the series of *N*-alkylated dyes, increasing the steric hindrance to charge transfer from the donor phenoxide fragment to the acceptor pyridinium ring by increasing the bulk of the *N*-substituent (methyl < *n*-butyl < 2-propyl), had little or no effect on the solvatochromic behaviour of the resulting dye. In the series of *N*-aryl pyridones, however, a small electronic effect was observed with electron donating substituents at the 4-position of the *N*-aryl substituent shifting the charge transfer band to lower wavelengths. This was especially evident in the case of the *N*-(4-oxyphenyl) derivative **4g** which absorbed at lower wavelengths than any other *N*-aryl or even *N*-alkyl analogue. This behaviour is at variance with the rather surprising observation made by Reichardt for the analogous systems **5**, where methylation of the strongly electron donating 4-oxyphenyl substituent had practically no influence upon the solvatochromic behaviour of these γ-vinylogous pyridones.



5 X = OMe, O$^-$

Table 1 Variation of the position of the charge transfer band of dyes **4** with solvent

	λ_{max}/nm						
Solvent	**4a**	**4b**	**4c**	**4d**	**4e**	**4f**	**4g**
Ethane-1,2-diol	417	423	420	435	441	438	399
Methanol	429	429	429	450	452	447	411
Ethanol	448	457	457	469	472	469	430
Propan-1-ol	457	469	472	481	490	484	439
Butan-1-ol	463	466	472	481	487	484	433
Propan-2-ol	469	469	484	490	502	493	442
Pentan-2-ol	490	505	505	514	520	514	445
Acetonitrile	499	535	535	532	511	526	481
Dimethyl sulfoxide	523	550	553	550	550	544	520
Dimethylformamide	535	565	565	559	556	553	481
Chloroform	532	558	547	538	545	535	445
Tetrahydrofuran	523	568	550	535	529	520	493

---

[*] To receive any correspondence.

This work was supported by the Directoria de Ciencia y Tecnologia (DICYT) of the Universidad de Santiago.

Techniques used: ^{1}H NMR, UV, elemental analysis

References: 10

Fig. 1: Solvatochromic behaviour of **4d** in polar solvents

Fig. 2: Experimental variation of the wavenumber of the CT band of **4a** with the solvent polarity

Fig. 3: Theoretical variation of the HOMO–LUMO energy gap of **4a** with polarity

Tables 2 and 3: Data for **3**

Received, 29th July 1997; Accepted, 3rd November 1997
Paper E/7/05480G

References cited in this synopsis

1 V. Gageiro, M. Aillon and M. C. Rezende, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 201.
2 C. Machado, M. G. Nascimento and M. C. Rezende, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2539.
3 M. C. Rezende, L. Silva and C. Machado, *J. Chem. Soc., Perkin Trans. 2*, 1995, 483.
4 M. C. Rezende, J. S. Galdames and C. Aliaga, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1055.
5 C. Reichardt, P. Milart and G. Schaefer, *Liebigs Ann. Chem.*, 1990, 441.