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The unexpected formation of novel carbonyl dyes

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Abstract

The synthesis of novel carbonyl dyes obtained from the reaction between α-hydroxylated acetonaphthones and 2-fluorobenzophenone in basic medium is reported. The novel structures were unambiguously established using UV–vis, IR, mass, ^1H, ^{13}C and 2D NMR spectroscopies and were very similar to the open forms of photochromic diarylnaphthopyrans.

Keywords: Carbonyl dyes; S_NAr; Spectroscopic characterization; Naphthopyrans; 2-Fluorobenzophenone; Synthesis

1. Introduction

The reaction between 1-hydroxy-2-acetonaphthone and benzophenone in the presence of sodium *tert*-butoxide is known to give, after reflux in HBr/HOAc, mainly 2,2-diphenylnaphthopyran-4-one an useful compound for the synthesis of photochromic naphthopyrans [1,2]. The product is formed only after acid treatment. The reaction involves a base catalysed addition of 1-hydroxy-2-acetonaphthone to benzophenone followed by dehydration and acid catalysed intramolecular 1,4-addition of the hydroxyl to the α,β-conjugated ketone (Scheme 1). This reaction gives relatively low yields, requires an excess of base and ketone, and is limited to diarylketones [3–6].

In an attempt to prepare some fluoro substituted 2,2-diphenylnaphthopyran-4-ones, precursors of photochromic naphthopyrans [7], we investigated the reaction of 1-hydroxyl-2-acetonaphthone with 2-fluorobenzophenone under the same reaction conditions but unexpectedly, after the usual work-up, a blue dye was obtained.

2. Results and discussion

The reaction of 1-hydroxyl-2-acetonaphthone **1** with 2-fluorobenzophenone **2**, in the presence of potassium *tert*-butoxide, in toluene under reflux afforded a red suspension that, after solvent evaporation, was treated with HCl/HOAc. Hydrolysis and CH_2Cl_2 extraction gave a deep blue solution. After column chromatography a blue dye was isolated in low yield. No traces of the possible fluoro substituted naphthopyran-4-one were detected. When dissolved in CH_2Cl_2, the blue dye was not extracted by a basic solution of NaOH (aq) indicating that it was not a phenol. Spectroscopic characterization of this new compound, including mono and bi-dimensional NMR techniques (DEPT, COSY, HMBC, HSQC) proved the highly conjugated structure **3** (Scheme 2), in accordance to the deeply blue solutions that are obtained with this compound.

In the infrared spectrum of the blue dye **3**, the main features were the lack of hydroxyl characteristic absorbances, the presence of a band at 1624 cm^{-1}, pointing to a conjugated carbonyl group possibly involved in intramolecular hydrogen bonding, and several bands between 1440 and 1590 cm^{-1} that could be assigned to aromatic carbon–carbon stretching. The HRMS displayed the molecular ion peak at *m/z* 348.1148 (100%), consistent with the molecular formula $C_{25}H_{16}O_2$ (calculated for $[C_{25}H_{16}O_2]^+$ 348.1150), and a prominent peak at *m/z* 271.08 (35%) corresponding to the loss of one phenyl group. Noteworthy was the absence of the fluorine atom in the structure.

The ^{13}C NMR spectrum showed 23 signals and DEPT experiments revealed 16 methine groups and 9 quaternary

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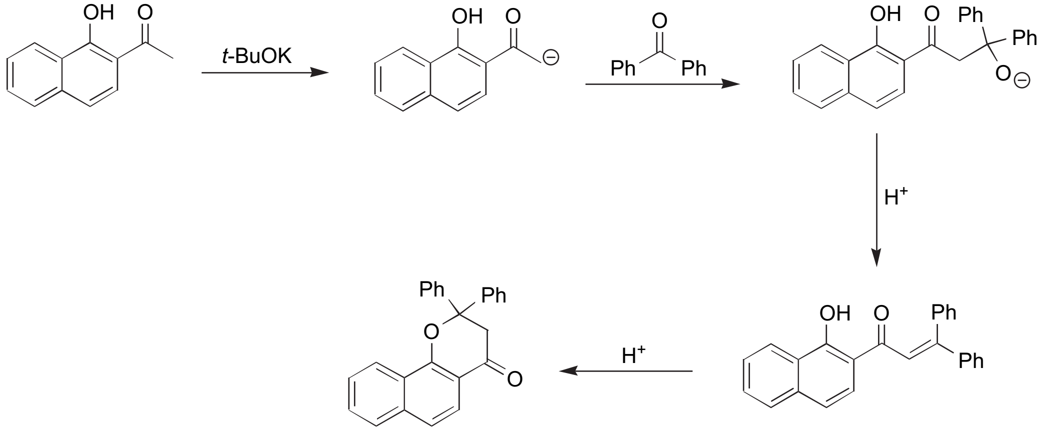
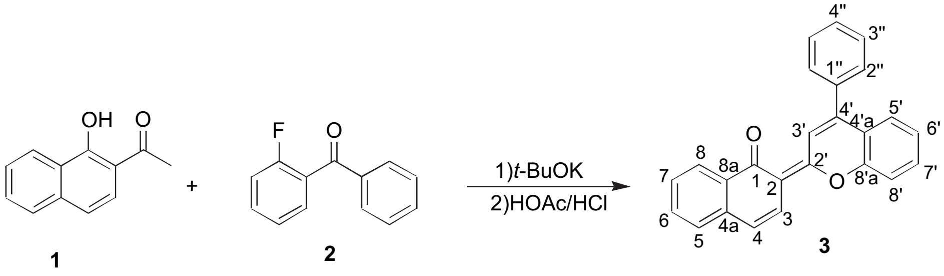


Scheme 1.



Scheme 2.

carbons (each methine signals at δ_C 128.98 and 128.77 correspond to 2 equivalent carbons of a phenyl group in the molecule). The quaternary carbons' resonances indicated the presence of a carbonyl group (δ_C 183.58) and unsaturated or aromatic carbons linked to oxygen atoms (e.g. δ_C 162.44 and 153.34). The presence of a fused benzene ring was deducted through the characteristic pattern observed in the ^{1}H NMR and ^{1}H−^{1}H COSY spectra that revealed one doublet

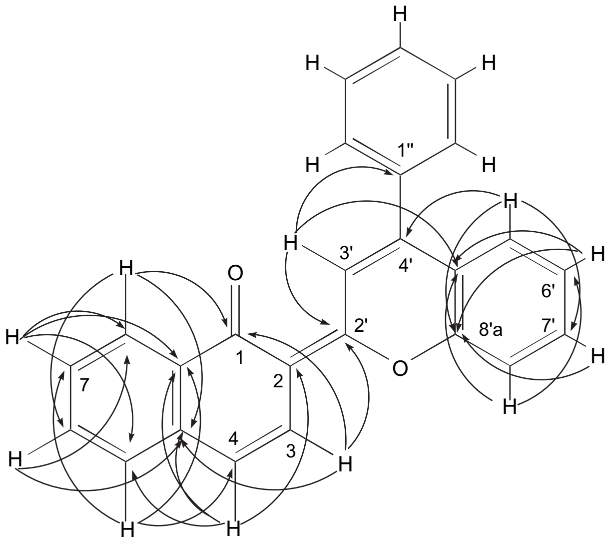


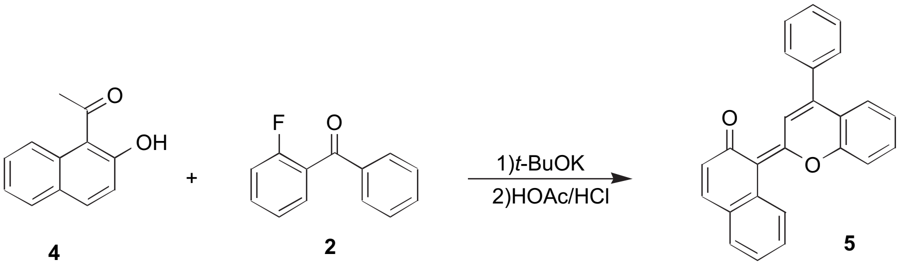
Fig. 1. Long-range C−H correlations obtained from HMBC.

Table 1
NMR spectral data for the blue dye **3**

Atom	^{1}H (*J* in Hz)	^{13}C	^{1}H−^{1}H COSY	HMBC
1	−	183.58, s		
2	−	111.21, s		
3	7.66, d (9.6)	123.18, d	H-4	C-1, C-2′, C-4a
4	6.73, d (9.6)	119.53, d	H-3	C-2, C-4a, C-5, C-8a
4a	−	137.78, s		
5	7.42, d (7.6)	127.25, d	H-6	C-4, C-7, C-8a
6	∼7.55[a]	131.84, d	H-5, H-7	C-4a, C-8
7	7.36, dd (7.5, 8.0)	126.38, d	H-6, H-8	C-5, C-8, C-8a
8	8.34, d (8.0)	126.90, d	H-7	C-1, C-4a, C-6
8a	−	132.59, s		
2′	−	162.44, s		
3′	9.12, s	120.74, d		C-2′, C-4′a, C-1″
4′	−	150.14, s		
4′a	−	121.38, s		
5′	∼7.55[a]	126.47, d		C-4, C-7, C-8′a
6′	7.25, dd (7.5, 7.6)	124.81, d		C-4′a, C-8′
7′	∼7.58[a]	132.03, d		C-8′a
8′	∼7.51[a]	117.12, d		C-4′a, C-6′
8′a	−	153.34, s		
1″	−	136.05, s		
2″ and 6″	∼7.52[a]	128.77, d		
3″ and 5″	∼7.62[a]	128.98, d		
4″	∼7.52[a]	129.54, d		

All ^{1}H−^{13}C connectivities were assigned by HMBC and HSQC and multiplicities were determined by DEPT experiments.

[a] Approximate central values due to overlapped signals.



Scheme 3.

at δ_H 8.34 (1H) correlated with a triplet at δ_H 7.36 (1H, $J_1 = 8.0$ Hz, $J_2 = 7.5$ Hz) that additionally was also correlated with an obscured signal, due to overlapping, centred at approximately δ_H 7.5 and correlated with a doublet at δ_H 7.42 (1H, $J = 7.6$ Hz). Besides those signals a downfield singlet at δ_H 9.12 (1H) and two correlated doublets at δ_H 7.66 (1H) and 6.73 (1H, $J = 9.6$ Hz) were relevant.

The key feature to establish the connectivity of these partial data was established by the long-range C−H correlations found in the HMBC spectrum (Fig. 1, Table 1). Cross-peaks between the carbonyl carbon (δ_C 183.58) and one proton of each non-intercorrelated doublets at δ_H 8.34 and 7.66 and the cross-peaks between these protons and the quaternary carbons at δ_C 132.59 and 137.78 pointed to the presence of a naphthalenone moiety. Additional information depicted in Fig. 1 allowed the unequivocal identification of the naphthalene-1(2*H*)-one nucleus. The identification of the 2-substituent was achieved through the cross-peaks between the proton δ_H 9.12 and the carbons at δ_C 162.44, 136.05 and 121.38.

Starting from 2-hydroxy-1-acetonaphthone **4**, and using the same procedure, we obtained a red dye that was purified only by recrystallization from CH_2Cl_2/hexane, since complete degradation was observed upon column chromatography using SiO_2 or Al_2O_3. The spectroscopic data are consistent with structure **5** (Scheme 3).

In CH_2Cl_2 or methanol, the blue dye **3** exhibits a large band in the visible spectrum with a maximum at 538 nm (ε 1.1×10^4), a sub-maximum at 577 nm (ε; 1.1×10^4) and two shoulders at 504 nm (ε; 0.83×10^4) and 630 nm (ε 0.50×10^4) (Fig. 2). The wavelength of maximum absorption of this compound was poorly sensitive to the solvent. In petroleum ether and ethyl acetate, hypsochromic shifts of 8 and 4 nm, respectively, were observed which are consistent with the low polarity of the proposed structure. The red dye **5** exhibits a large absorbance band with a maximum at 509 nm (ε; 1.0×10^4).

The presence of a fluorine atom in the benzophenone nucleus led to an unexpected compound that must be formed through a different mechanism to that outlined in Scheme 1. We suggest that enolate **A**, formed by reaction of hydroxyacetonaphthone **1** with the *tert*-butoxide, substitutes the fluorine atom in the 2-fluorobenzophenone through a nucleophilic aromatic substitution reaction, leading to a conjugated enol. In basic medium this compound is probably in the anionic form **B**. Protonation of this intermediate, followed by ring closure, leads to alcohol **C** that by acid dehydration should afford dye **3** (Scheme 4). It should be noted that the dye is structurally very similar to the unstable coloured open form of photochromic naphthopyrans. The structure is stabilized through a chemical bond between carbon 2′ and oxygen 1′ atoms that does not exist in those short-lived species.

3. Experimental

The reagents were obtained from Aldrich and were used as supplied. Solvents were of analytical grade. The reactions were monitored by thin-layer chromatography on aluminum plates precoated with Merck silica gel 60 F254 (0.25 mm). Melting points were determined in capillary tubes and are uncorrected. The new compounds were determined to be >95% pure by ^{1}H NMR spectroscopy. The ^{1}H and ^{13}C NMR spectra were recorded at 298 K in $CDCl_3$ using a Bruker ARX400 spectrometer (at 400.13 and 100.62 MHz). Chemical shifts (δ) were reported in parts per million and coupling constants (J) in hertz. Resonance multiplicities for ^{13}C were established via the acquisition of DEPT spectra. Heteronuclear ^{1}H−^{13}C HSQC and HMBC experiments were carried out using standard procedures. UV−vis spectra were recorded on a CARY 50 Varian spectrophotometer. IR spectra were recorded on a Perkin−Elmer FTIR 1600 spectrometer using KBr disks (wavenumbers in cm^{-1}). Electron impact mass spectra were measured on a AutoSpecE spectrometer.

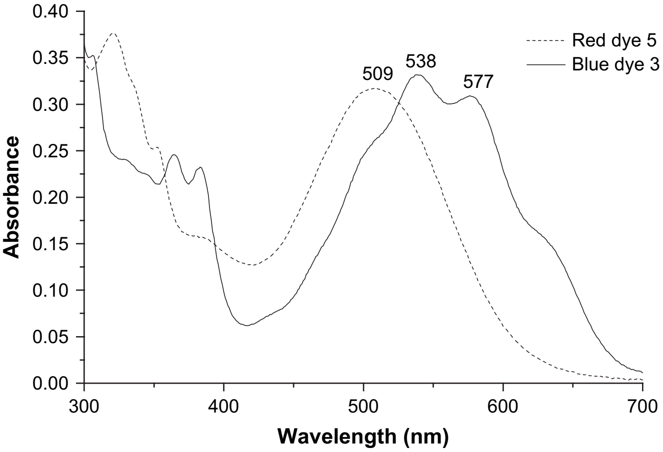
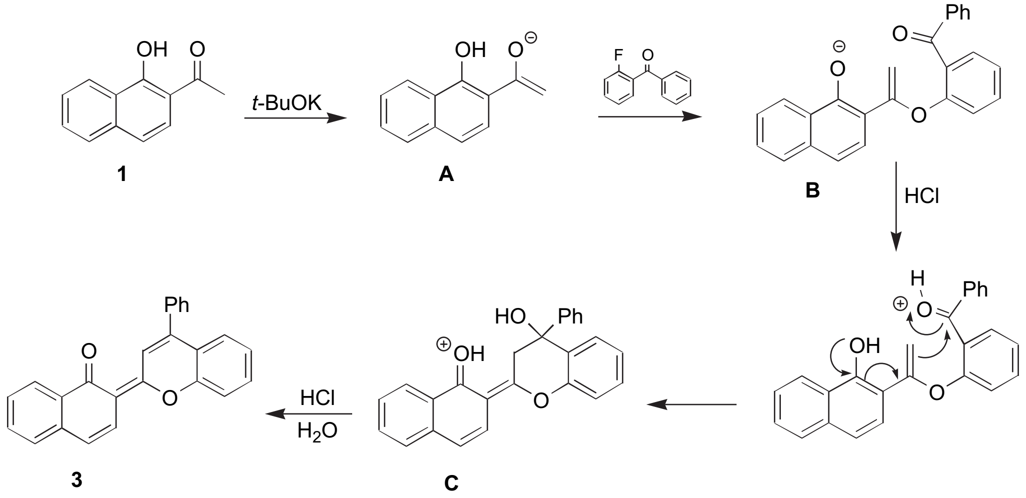


Fig 2. UV−vis spectra of compounds **3** and **5** (3.1×10^{-5} M, CH_2Cl_2).



Scheme 4.

3.1. Synthesis of (2E)-2-(4′-phenyl-2H-chromen-2′-ylidene)naphthalene-1(2H)-one **3**

1-Hydroxy-2-acetonaphthone (1.0 mmol), 2-fluorobenzophenone (1.0 mmol) and potassium *tert*-butoxide (5 mmol) in toluene (15 ml) were refluxed for 6 h. A red suspension was produced and after cooling to room temperature the solvent was evaporated leaving an orange solid to which CH_3COOH (5 ml) and HCl conc (3 ml) were added. After heating for 10 min a deep red solution was obtained that was poured over 100 ml of water. The blue suspension was extracted with CH_2Cl_2 (4 × 25 ml) and the organic extracts were washed with water (3 × 100 ml) and dried over anhydrous Na_2SO_4. Solvent evaporation gave a blue residue that was purified by column chromatography (5–10% ethyl acetate/petroleum ether) on silica gel 60 (70–230 mesh) and 20 mg of the compound was obtained. Yield 5.7%. M.p. 155–158 °C. IR: 3050, 2923, 2852, 1624, 1593, 1541, 1505, 1468, 1371, 1315, 1273, 1235, 955, 923. For ^{1}H and ^{13}C NMR data see Table 1. MS, *m*/*z* (%): 348 (100), 331 (25), 289 (10), 271 (40). Exact mass for $C_{25}H_{16}O_2$: 348.1150; found: 348.1148.

3.2. Synthesis of (1E)-1-(4′-phenyl-2H-chromen-2′-ylidene)naphthalene-2(1H)-one **5**

The same procedure was used except that 2-hydroxy-1-acetonaphthone was used instead of 1-hydroxy-2-acetonaphthone and the final red residue was purified through recrystallization from CH_2Cl_2/petroleum ether and 15 mg of compound **5** was isolated. Yield 4.3%. M.p. 157–160 °C. IR: 3050, 2930, 1623, 1596, 1558, 1522, 1456, 1345, 1278, 1211. ^{1}H NMR ($CDCl_3$): 8.86 (s, 1H, H-3′), 8.36 (d, 1H, *J* 8.0), 8.26 (d, 1H, *J* 8.0), 8.17 (d, 1H, *J* 8.0), 8.10 (m, 2H), 7.99 (d, 1H, *J* 9), 7.85–7.55 (m, 8H), 7.47 (t, 1H, *J* 7.6). MS: *m*/*z* (%): 348 (80), 331 (90), 289 (20), 273 (35), 271 (100), 194 (20). Exact mass for $C_{25}H_{16}O_2$: 348.1150; found: 348.1147.

4. Conclusions

Novel carbonyl dyes were obtained from the reaction of hydroxylated acetonaphthones with 2-fluorobenzophenone and the structures were established using spectroscopic techniques. A mechanism involving a nucleophilic aromatic substitution followed by acid catalysed ring closure and dehydration was proposed. This novel class of dyes is similar to the coloured open forms of photochromic naphthopyrans stabilized through an oxygen bridge between carbons 2′ and 8′a.

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