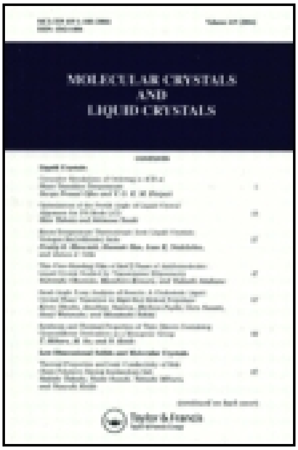

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Photochromism of Some Heterobenzopyrans

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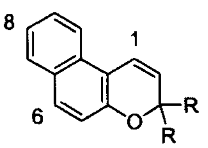
Some novel heterobenzopyrans have been synthesised and their photochromic properties are discussed.

Keywords: Photochromism; heterobenzopyrans; nmr spectroscopy

INTRODUCTION

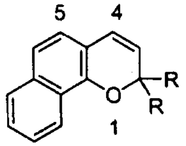
The synthesis and photochromic properties of naphthopyrans has been the subject of several reviews.[1a - c] Much of the early work focused on the synthesis of 3-spirocycloalkane- and 3-alkyl-3-aryl-3*H*-naphtho[2,1-*b*]pyrans (1).[2] The move to 3,3-diaryl substitution led to significant improvements in fatigue resistance and intensity of photo-generated colour.[3] The isomeric 2,2-diaryl-2*H*-naphtho[1,2-*b*]pyrans (2) were initially much less studied probably as a consequence of the very slow rate of fade of the photo-generated colour when compared to (1). However, this problem of slow fade was addressed in our research disclosure [4] which demonstrated that a substituent at the 5-position of (2) brings about a dramatic increase in the rate of fade, such that 2*H*-naphtho[1,2-*b*]pyrans are often the compounds of choice for imparting photochromic properties to ophthalmic lenses.[5]

The intense activity directed towards the synthesis of novel 5-substituted photochromic 2*H*-naphtho[1,2-*b*]pyrans stimulated by this disclosure [4] has led to a variety of substituted naphthopyrans [5], pyrans fused to carbocyclic rings [6], indenopyrans [7] and some heterobenzopyrans e.g. pyranocarbazoles [8] and thieno- and furobenzopyrans.[9] We now report some of our earlier findings on the synthesis and photochromic properties of some heterobenzopyrans.



3*H*-naphtho[2,1-*b*]pyran

(1)

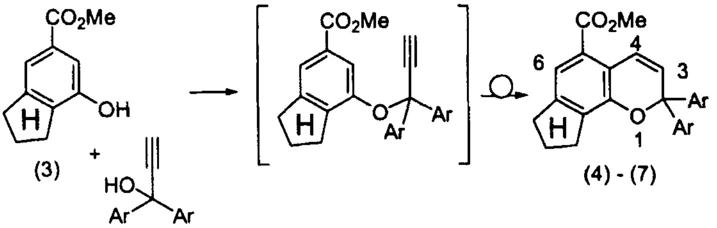


2*H*-naphtho[1,2-*b*]pyran

(2)

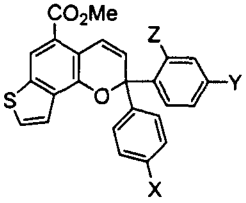
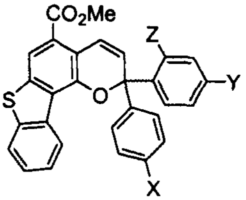
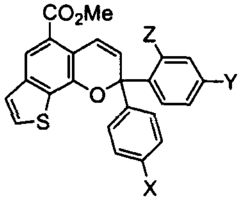
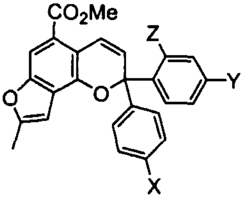
DISCUSSION

The most convenient synthetic route to heterobenzopyrans (4) – (7) relies upon the one pot, acid-catalysed etherification of a heterofused phenol (3) with a 1,1-diarylprop-2-yn-1-ol to afford an ether, which readily undergoes a Claisen rearrangement followed by sigmatropic H-shifts and a subsequent electrocyclic ring closure to afford (4) – (7) (Scheme 1, Table 1). A range of heterocyclic phenols was readily obtained by extending the established Stobbe condensation - ring closure route to naphthols from an aromatic aldehyde [10] to heteroaromatic aldehydes.



Scheme 1

Table 1. Spectroscopic Data for Heterobenzopyrans (4) – (7)

Structure[1]	No.	X	Y	Z	λ_{max}[2] (nm)	$t_{1/2}$ (sec)
	4a	MeO	MeO	H	503	640
	4b	MeO	MeO	MeO	504	1550
	4c	Me_2N	Me_2N	H	605	<0.5
	4d	Me_2N	Me_2N	Me	600	2
	4e	Morph[3]	H	H	545	<0.5
	4f	Morph[3]	H	Cl	548	270
	5a	MeO	MeO	H	470	620
	5b	MeO	MeO	MeO	468	890
	5c	Morph[3]	H	H	533	43
	6a	MeO	MeO	H	498	<0.5
	6b	MeO	MeO	MeO	507	15
	7a	MeO	MeO	H	520	<0.5
	7b	MeO	MeO	MeO	523	11

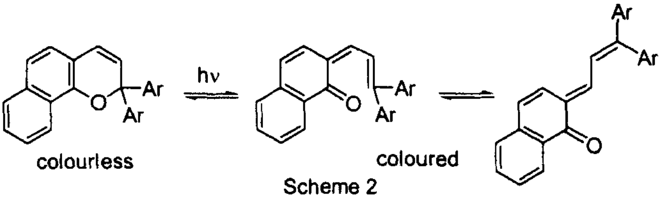
Notes

1. All new compounds were fully characterised by IR, UV-Vis, ^1H and ^{13}C NMR, HRMS and elemental analysis.[11]
2. λ_{max} and $t_{1/2}$ were obtained for solutions of (4) – (7) in spectroscopic grade toluene at 20 °C after irradiation to a constant intensity.
3. Morph represents a morpholino substituent.

The signal for 3-H in the ^1H NMR spectra of (4) – (7) appears as a doublet in the relatively narrow range δ 6.1 to δ 6.5 with $J_{3,4}$ = 10.2 Hz.

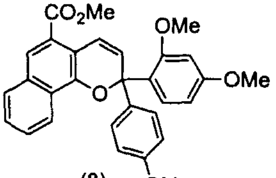
4-H Resonates downfield of 3-H at ~ δ 7.6 as a consequence of its benzylic disposition and is relatively unaffected by the *peri* carbonyl function. The low field shift of 11-H of (5), δ 8.8, is noteworthy and results from the interaction between 11-H and the pyran ring oxygen atom. The remaining signals in the ^{1}H NMR spectrum of (4) – (7) appear in the regions expected for the individual structural types and in accord with the nature of the substituents.

The photochromic process of the naphtho[1,2-*b*]pyran unit is well documented and relies upon a reversible 6π-electrocyclic ring opening of the pyran ring under UV irradiation to afford an intensely coloured dienone that can interconvert to a number of isomers and rotamers (Scheme 2).



Scheme 2

In order to assess the influence of hetero-ring fusion, the model naphthopyran (8) with λ_{max} 490 nm and $t_{½}$ 450 sec. was used.



(8)

A direct comparison of the photochromic properties of the 2,2-di(4-methoxyphenyl) derivatives of the four hetero-fused systems (4a – 7a) is only of qualitative value since the lifetimes of the ring opened forms of (6a) and (7a) were short. Nonetheless, it is clear that there is a major difference in stability of the coloured forms of the two thienobenzopyran isomers (4a) and (6a). Similarly, the furo- and thieno-[2,3-*h*]benzo-pyrans (4a) and (7a) exhibit vastly different behaviour following irradiation.

In order to obtain more meaningful spectroscopic data, an *o*-methoxy substituent was additionally incorporated into one of the *gem.* aryl rings. It is well established that the presence of an *ortho*-substituent on a 3-aryl substituent decreases the rate of ring-closure of the coloured form.[12]

The data in Table 1 for compounds (4b), (5b), (6b) and (7b) further substantiate this feature. It is noted that an *o*-methoxy group has minimal effect on λ_{max}.

A thiophene ring, irrespective of its mode of fusion, brings about a red shift of *ca*. 15 nm of λ_{max} in accord with the π-electron rich aromatic nature of the thiophene ring [(4b), (6b) *vs*. (8)]. However, the 100× slower fade of the [2,3-*h*] isomer (4b) compared with the [3,2-*h*] analogue (6b) is of greater significance.

Benzannulation results in a blue shift of 36 nm [(4b) *vs*. (5b)] but also increases the rate of fade.

The least aromatic of the four systems, the furobenzopyran (7b), provides for the largest bathochromic shift (λ_{max} 523 nm) and fastest fading photo-generated coloured species ($t_{½}$ = 11 sec.).

The influence of substitution in the *geminal* diaryl function by groups other than methoxy on the photochromic properties of the thieno[2,3-*h*][1]benzopyrans (4) was also explored. The introduction of NMe_2 groups in the *para* positions of the diaryl groups (4c) resulted in a dramatic decrease in $t_{½}$ such that λ_{max} could only be obtained on cooling the solution. The incorporation of an *ortho* methyl group (4d) increased $t_{½}$ to 2 sec. with a λ_{max} of 600 nm. The observation that each NMe_2 function induces a bathochromic shift of λ_{max} of ~ 50 nm is in accord with our previous observations.[1c]

A cyclic amino function exerts a similar effect to a dimethylamino group, with one morpholine substituent bringing about a red shift of 42 nm in (4e) relative to (4a) and of 63 nm in the benzologue (5c) *vs*. (5a). The enhanced kinetics of ring closure associated with a 4-aminophenyl group and its modification by an *ortho* substituent [see (4d)] are again apparent.

CONCLUSIONS

Some novel photochromic heterobenzopyrans have been synthesised. Fused 5-membered heterocycles bring about a red shift of λ_{max}. The location of a fused thiophene ring and the nature of the heteroatom have a profound effect on the rate of fade of the photo-generated forms.

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[11] E.g. **Methyl 2,2-di(4-methoxyphenyl)thieno[2,3-*h*][1]benzopyran-5-carboxylate (4a)** (59%) as colourless micro-crystals after elution from silica with 30 % ethyl acetate in hexane and recrystallisation EtOAc and hexane, m.p. = 95.0 – 97.0 °C; ν_{max} (KBr) 1715, 1609, 1511, 1280, 1251, 1036; δ_H ($CDCl_3$) 3.75 (6H, s, OMe), 3.89 (3H, s, CO_2Me), 6.14 (1H, d, *J* 10.3, 3-H), 6.81 (4H, m, Ar-H), 7.36 (4H, m, Ar-H), 7.46 (1H, d, *J* 5.5, 7-H), 7.55 (1H, d, *J* 5.4, 8-H), 7.64 (1H, d, *J* 10.3, 4-H), 8.05 (1H, s, 6-H) (Found: C, 70.6; H, 4.8; S, 7.0; MH^+, 459.1261. $C_{27}H_{22}O_5S$ requires C, 70.7; H, 4.85; S, 7.0 %; MH^+, 459.1266).

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