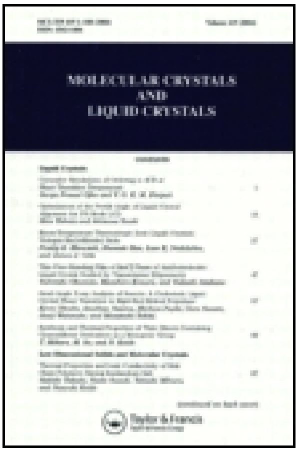

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Structure-Property Relationship of Heterofused Benzopyran

Anil Kumar [a]

[a] PPG Indusmes, Inc., 440 College Park Drive, Monroeville, PA, 15146, USA

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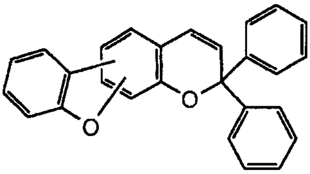
STRUCTURE-PROPERTY RELATIONSHIP OF HETERO-FUSED BENZOPYRAN

Anil Kumar
PPG Industries, Inc., 440 College Park Drive, Monroeville, PA 15146 USA

Abstract: A series of photochromic diaryl benzopyrans fused with benzofuran have been prepared and tested for photochromic performance. The four isomeric hydroxydibenzofurans were coupled with (un)substituted 1,1-diphenyl propargyl alcohols. The resulting photochromic products show bathochromic shifts in the UV and broad bands in the visible spectra compared to 2,2-diaryl benzopyrans (2,2-diarylchromenes). It has also been found that the position of the benzofuran fusion has a profound effect on the visible spectrum and fade rate. In addition to structure-property relationships, the synthesis of these compounds is discussed.

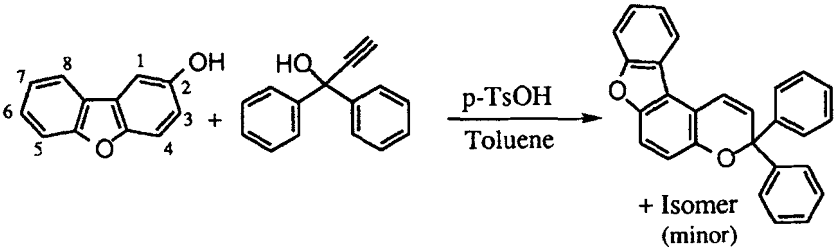
INTRODUCTION

The photochromism of 2,2-Diarylbenzopyrans, also commonly known as 2,2-diarylchromenes, was first studied by Ralph Becker.[1] Becker suggested their use in applications in which a sunlight induced reversible color change or darkening is required even though photochromic benzopyrans have little utility due to their weak response under solar illumination. With the goal of improving the sunlight induced photochromic response of benzopyrans, some novel hetero(benzofuro)-fused benzopyran derivatives were prepared and their properties studied.



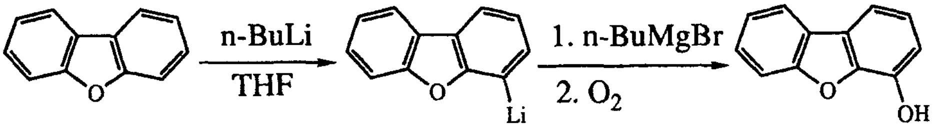
EXPERIMENTAL

The preparation of photochromic compounds was achieved by coupling a hydroxydibenzofuran and a propargyl alcohol in toluene solvent using a catalytic amount of *p*-toluenesulfonic acid (Scheme I).



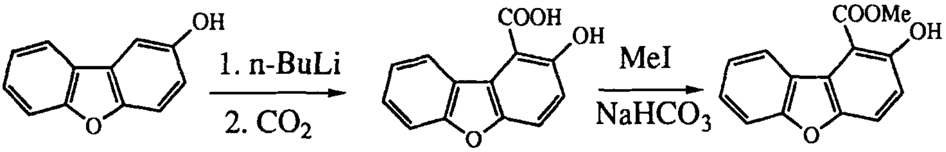
Scheme I Synthesis of a benzofuro- fused benzopyran

2-Hydroxydibenzofuran was purchased from Aldrich while 1-hydroxy, and 3-hydroxydibenzofuran were obtained from Chroma Chemicals, Inc.[2] 4-Hydroxy dibenzofuran was prepared by lithiation of dibenzofuran with n-butyl lithium at the 4 position followed by oxidation with oxygen in the presence of n-butyl magnesium bromide.[3] This process gave a 50% conversion to 4-hydroxy dibenzofuran which was separated from unreacted dibenzofuran by the base extraction.



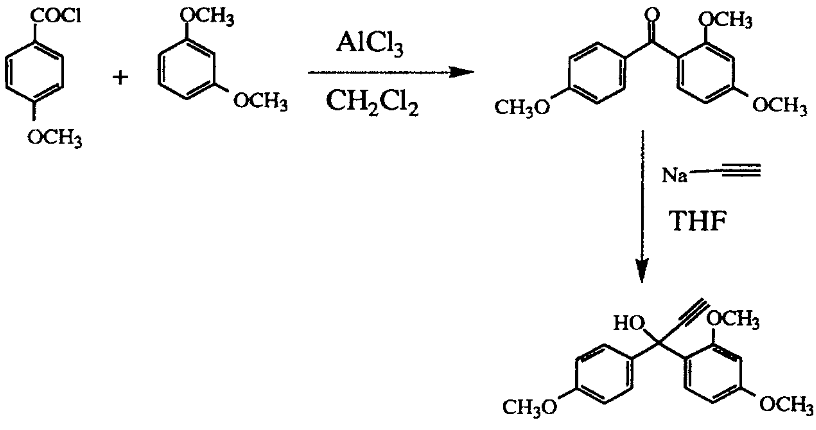
Scheme II Synthesis of 4-hydroxydibenzofuran

2-Hydroxydibenzofuran-1-carboxylic acid was prepared by metalation of 2-hydroxy dibenzofuran with 2.2 equivalents of n-butyllithium followed by carboxylation with carbon dioxide.[4] Hydrolysis of the mixture gave a 70% yield of carboxylic acid. The acid was esterified with methyl iodide in the presence of sodium bicarbonate using dimethylformamide as the solvent.



Scheme III Synthesis of 1-methoxycarbonyl-2-hydroxydibenzofuran

Substituted and unsubstituted propargyl alcohols were prepared by reacting the corresponding benzophenone with sodium acetylide in dry tetrahydrofuran. The benzophenone derivatives were either purchased or prepared by Friedel-Crafts methods using an appropriately substituted or unsubstituted benzoyl chloride and a commercially available substituted benzene compound.[5]



Scheme IV Synthesis of a propargyl alcohol

Table 1 summarizes the yields of the products obtained from the coupling reaction between hydroxydibenzofuran and propargyl alcohols. Where indicated, an isomer of the indicated benzofuro-fused benzopyran was also obtained as a side product.

As an example of the general synthetic route, the preparation of compound IV is outlined in detail. The detailed synthesis of other compounds can be found in the literature.[6]

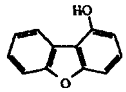
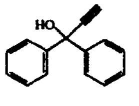
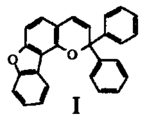
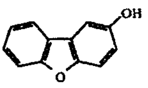
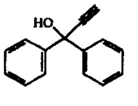
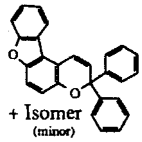
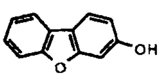
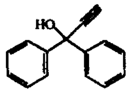
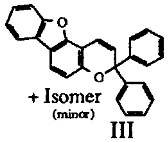
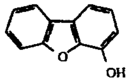
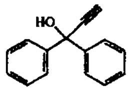
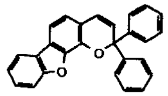
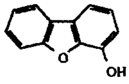
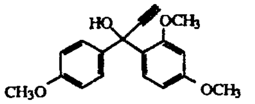
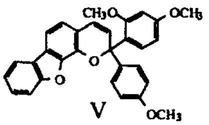
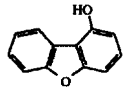
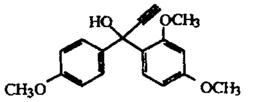
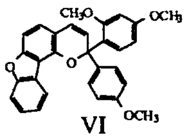
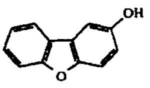
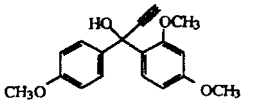
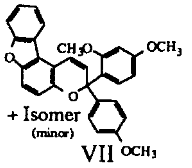
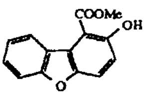
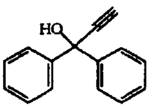
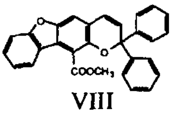
Preparation of 4-hydroxydibenzofuran

Dibenzofuran (16.8 grams, 0.1 moles) was dissolved in 200 ml of dry ethyl ether and stirred under argon at room temperature. n-Butyl lithium (125 ml (0.2 moles), 1.6 molar solution in hexane) was added dropwise and the mixture refluxed for 18 hours. The mixture was cooled to room temperature and 0.1 M of n-butyl magnesium bromide was added dropwise while maintaining the temperature at 25° C. The mixture was stirred at room temperature for 3 hours. The reaction temperature was lowered to 0° C with an ice bath. Oxygen was admitted over the surface of the stirred solution for 3 hours. The hydrolysis was done by slow addition of ice followed by dilute HCl with stirring for 10 min. The quenched mixture was extracted with diethyl ether. The phenolic product was extracted from the organic layer with a 10% NaOH solution. Acidification of the basic solution produced an oily phenolic compound which solidified after sitting for a few hours. The solid was filtered and air dried. The dry solid (used directly in the next stage) was 95% pure (% area by LC) and weighed 11 grams.

Preparation of 2,4,4'-trimethoxybenzophenone

1,3-Dimethoxy benzene (10 gram, 0.073 moles) and 12.5 gm (0.073 moles) of *p*-anisoyl chloride were mixed in 100 ml of anhydrous methylene chloride and stirred at room temperature. To this stirred solution 12.5 gm (0.092 moles) of anhydrous aluminum chloride was slowly added. After 3 hours of stirring, the reaction mixture was poured into a dil. HCl/ice mixture and stirred for 15 minutes. The mixture was extracted with methylene chloride. The organic layer was separated and washed with 10% NaOH solution followed by distilled water. The organic layer was separated and dried over anhydrous magnesium sulfate. Evaporation of solvent produced an oily product which crystallized by adding a small amount of hexane and letting it sit overnight. Filtering and acidification yielded 21 grams of product.

Table I : Summary of the synthesis of hetero- fused benzopyrans

Phenol	Propargyl Alcohol	% Yield	Product
		39	 I
		40	 + Isomer (minor) II
		49	 + Isomer (minor) III
		29	 IV
		39	 V
		47	 VI
		64	 + Isomer (minor) VII
		47	 VIII

General procedure for the preparation of 1,1 diaryl-2-propyn-1-ols.

Diaryl ketone (0.27 Moles) was dissolved in dry tetrahydrofuran and stirred at room temperature. To this stirred solution a 10% molar excess of sodium acetylide (Aldrich, or Farchan, 18% slurry in xylene/mineral oil) was added and stirred overnight at room temperature. The reaction mixture was poured into a dil HCl/ice mixture and extracted with diethyl ether. The organic layer was separated, washed, and dried over anhydrous sodium sulfate. Evaporation of the solvent yielded the crude product as an oil. Generally, the crude alcohol obtained was used, as is, for the next step, If necessary column chromatography can be used for purification.

General procedure for the preparation of 2,2 diaryl-[2H]-benzo(b)furo [3,2-h] [1]benzopyran

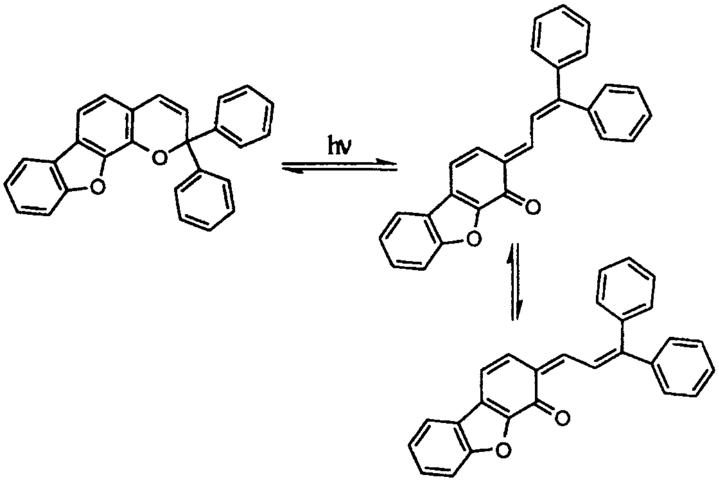
4-Hydroxy dibenzofuran (5.5 grams, 0.03 moles (Aldrich)) and the crude propargyl alcohol obtained as described above were mixed in 200 ml of toluene and stirred at room temperature. *p*-toluenesulfonic acid (100 mg) was added as catalyst and stirring was continued for 4 hours. The reaction was monitored by TLC and LC. Upon completion, the reaction mixture was poured into water. The organic layer was separated and washed successively with 10% NaOH and water. The organic layer was dried over anhydrous sodium sulfate and concentrated. The residue obtained was passed through a silica gel column using chloroform/hexane (1:3) as eluant. The fractions containing the photochromic compound were combined and the solvent evaporated. The resulted oily product was induced to crystallize from hexane yielding 2.5 grams of product.

Sample preparation The photochromic compounds were incorporated into an ethyl cellulose resin by the following procedure. About 30 milligrams of the photochromic compound was added to 2.0 grams of a 10 weight percent ethyl cellulose solution in toluene. The photochromic compound was dissolved by warming and stirring on a steam bath. Approximately 2.0 grams of the resultant solution was deposited on the edge of a 75 by 25 millimeter (mm) glass slide. Using a draw down bar, a 0.2 mm layer of photochromic resin solution was placed evenly on the slide and permitted to dry.

Physiochemical characterization and photochromic evaluation The UV-VIS spectra were measured on a Varian Cary 3 UV-Visible Spectrophotometer. The photochromic properties were measure on an optical bench. The Δ OD/Min., which represents the sensitivity of the photochromic compound's response to UV light, was measured over the first five seconds of UV exposure, then expressed on a per minute basis. The Bleach Rate T 1/2 (sec.) is the time interval in seconds for the absorbance of the activated form of the benzopyran in the test sample to reach one half the highest absorbance at room temperature . The equilibrium or steady state response was measured as a change in optical density (ΔOD). The λmax value, which is the maximum absorption of the activated (colored) form of the photochromic compound in ethyl cellulose resin, may occur at one or two wavelengths reported as Band A and Band B in Table 2.

RESULTS AND DISCUSSION

On exposure to UV light, benzofuro- fused benzopyrans (e.g. IV) also undergo a reversible ring opening process of the pyran ring (see Scheme V) It is speculated that interchangeable open forms are responsible for the observed color. In Scheme V the open forms are drawn as quinoidal structures (rather than zwitterionic species which are believed to be the structure of the colored form of the spiroxazines[7]). Although the nature of the open forms of pyrans are relatively unknown, low temperature NMR studies tentatively supports a quinoidal structure.[8]



Scheme V: Photochromic process in heterofused- benzopyran

Fig 1 shows the visible spectrum for compound I after irradiation. The visible spectrum is composed of two peaks. The one which lies between 400 and 500 is strong (band A) and the other which lies between 500 and 700 is very broad and weak(band B). Absorption maxima and photochromic properties are summarized in Table 2. The position of band A and band B appears to depend on the orientation of the fusion of the heterocycle to the benzopyran (see Table 2, compound I, II, III and IV). The observed color depends on the position, ratio, and broadness of the bands. For example compound I has a very strong band A at 409 nm and medium broad band B at 536 nm. When activated the compound is yellow-brown in color. On the other hand compound III has a band A at 434 nm and band B at 590 nm. When activated it appears a green-brown in color.

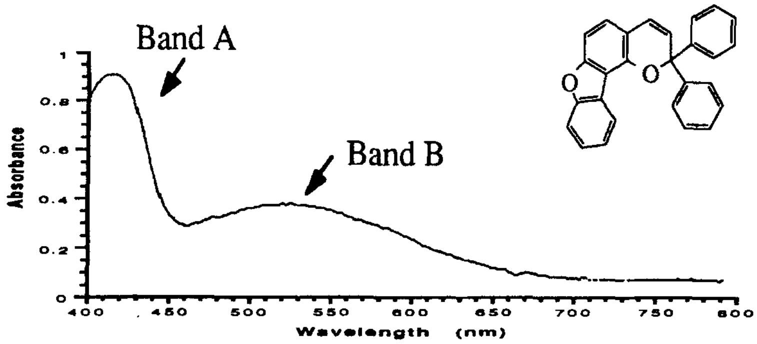


Fig. 1: Visible spectrum of compound I

Substitution on the phenyl groups has the same effect as is observed in the naphthopyran family. Ortho substitution tends to slow the fade rate and increase the optical density.[9] This effect is demonstrated by compounds I vs VI and II vs VII.

Table 2 : Performance of photochromic compounds in ethyl cellulose

Compound Number	λ max Band A	 Band B	SENSITIVITY ΔOD / MIN.	ΔOD SAT	BLEACH T1/2 Sec.
I†	409	536	----	----	----
II	438	522	0.42	0.18	85
III†	434	590	----	----	----
IV	418	430	0.05	0.21	>800
V	461	550	0.15	0.51	>800
VI	443	530	0.03	0.20	>800
VII	457	527	0.47	0.54	630
VIII	460	525	0.16	0.33	489

† : Fade rate is too fast to measure the performance at room temperature

CONCLUSION

Several novel benzofuro- fused benzopyrans were synthesized and their photochromic properties were studied. These compounds have interesting visible absorption spectra composed of two peaks. In addition, the position of hetero- fusion has been found to have a profound effect on visible spectra and fade rates.

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