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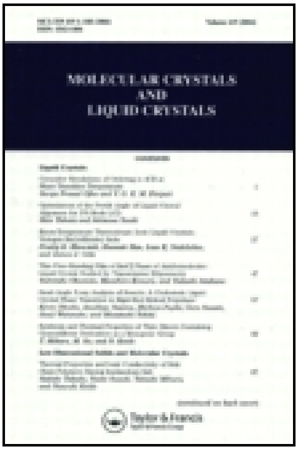

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Photochromism of Diarylnaphthopyrans

Barry Van Gemert [a] , Maria Bergomi [a] & David Knowles [a]
[a] PPG Industries, Monroeville, PA, 15146, USA

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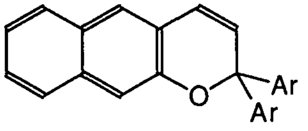
PHOTOCHROMISM OF DIARYLNAPHTHOPYRANS

BARRY VAN GEMERT, MARIA BERGOMI, AND DAVID KNOWLES
PPG Industries, Monroeville, PA, 15146 USA

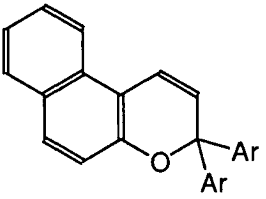
Abstract A series of 3,3-diaryl-3H-naphtho[2,1-b]pyrans were prepared and their photochromic properties measured in plastic matrix. The influence of a variety of substituents on color, intensity, and fade were studied.

BACKGROUND

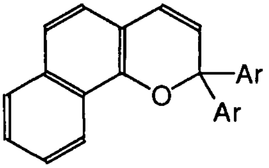
There are three possible diaryl naphthopyran isomers (I, II, III) with the aryl groups α to the pyran oxygen.



I



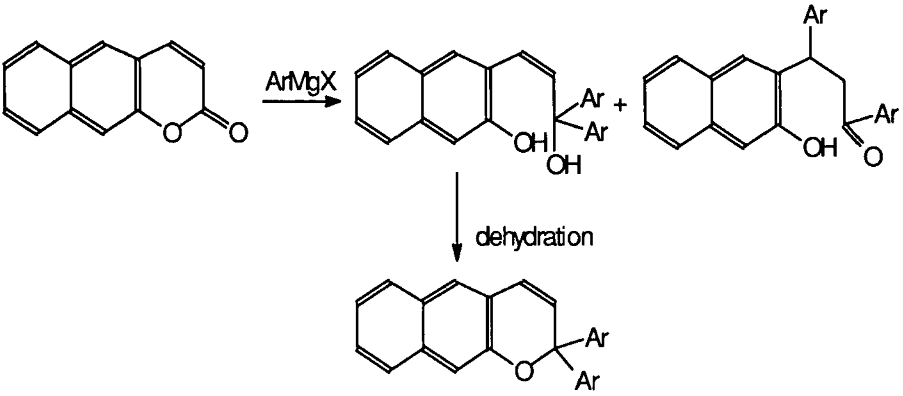
II



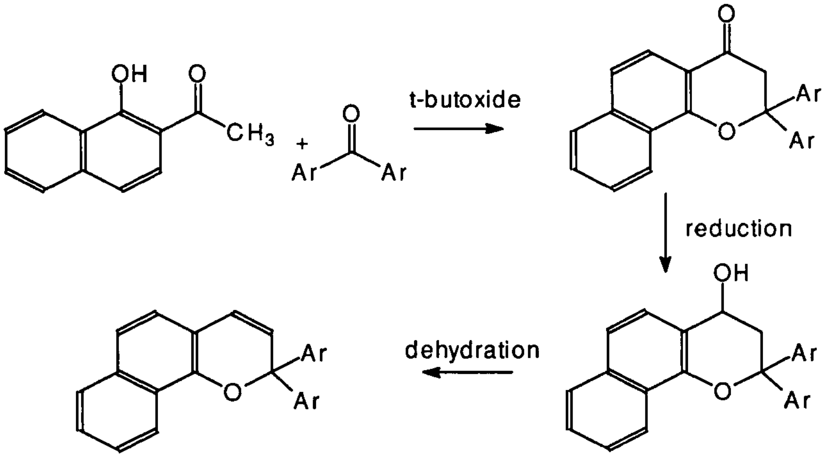
III

The first attempt at the synthesis of such a compound was made by Wizinger and Wenning[1] in 1940 when they reacted 2-hydroxy-1-naphthaldehyde and 1,1-diphenylethylene in acetic acid saturated with HCl. The solid isolated (mp 194-195°) was not the expected 3,3-diphenyl-3H-naphtho [2,1-b]pyran but rather, as was later shown in 1960 by Livingstone et al[2], a condensation product of the desired pyran and a second molecule of diphenylethylene. Unfortunately in the interim (1954), Hirshberg and Fischer[3] while studying the photochromic and thermochromic properties of pyrans, found the Wizinger and Wenning product to be non-photochromic. It was not until the work of Becker in the late 1960's[4] and early 1970's[5] set the record straight and the novel properties of this class of compounds became widely known.

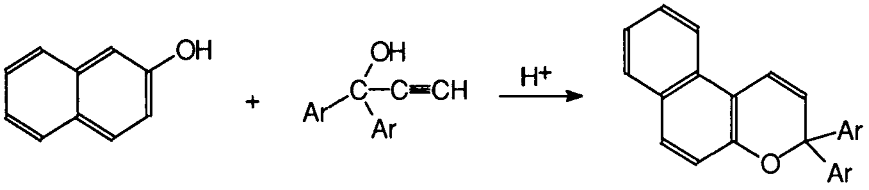
At least three synthetic routes to diaryl naphthopyrans have been reported in the literature. Reaction of two moles of an aryl grignard with a benzocoumarin followed by dehydration is a general method but the yields are usually low due to the occurrence of some 1,4-addition[6].



o-Hydroxyacetonaphthones can be condensed with benzophenone in the presence of sodium t-butoxide to give an intermediate benzochromanone[7]. Whereas such a condensation with an aliphatic ketone proceeds in near quantitative yield using basic catalysts such as pyrrolidine[8], benzophenones require the stronger condensing agent and yields are extremely poor. Two additional steps (reduction and dehydration) are required to prepare the dihydropyran by this method.

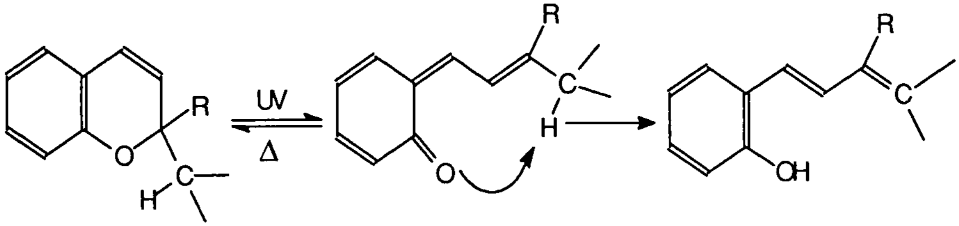


The preferred method, owing to its simplicity, is the acid catalyzed condensation of a naphthol with a 1,1-diaryl-2-propyn-1-ol[9].



In a variation of this method a titanium naphthoxide is reacted with a β-aryl cinnamaldehyde[10]. The two reactions are related in that the cinnamaldehydes are possibly intermediates in the reaction pathway of the propynols. Unfortunately this simple one step method can not be used to prepare 2,2-diaryl-2H-naphtho[2,3-b]pyrans (compounds of general structure 1 above).

Although organic photochromic compounds have been known for decades, their tendency to fatigue, that is their tendency to lose their ability to reversibly switch from the colorless form to the colored form and back again, has limited their utility. Spiropyrans are in general considered more fatigue prone than the indolino spirooxazines. Spiropyrans bearing a nitro group photo degrade very rapidly due to the involvement of triplet states in the coloration process. Non nitro containing compounds such as the spiro indolino naphthopyrans have better stability but poor colorability[11]. With pyrans not containing a spiro heterocyclic group, it has been shown that if the substituent on the carbon α to the pyran oxygen contains an α hydrogen then the compounds rapidly fatigue via a 1,7-sigmatropic hydrogen shift[12].



Heller[9] has attempted to short circuit this fatigue mechanism by introducing a spiro adamantane group at the position α to the pyran oxygen. A 1,7-hydrogen shift in the open (colored) form of these compounds and creation of a bridgehead double bond would be a violation of Bredt's rule. Likewise, naphthopyrans substituted with aryl groups α to the pyran oxygen have no hydrogens available to undergo the 1,7 shift and should, at least in theory, be less fatigue prone than pyrans that are capable of undergoing the sigmatropic rearrangement.

MATERIALS AND METHODS

Photochromic naphthopyrans were prepared by the acid catalyzed reaction of naphthols with diaryl propargyl alcohols. In general they were purified by column chromatography and crystallization. For testing purposes the compounds were imbibed into polymer prepared from CR-39^{R} diethyleneglycol bis(allyl carbonate) monomer via a paper transfer technique. Photochromic properties were measured at room temperature on an apparatus employing an Ealing Triangular optical bench equipped with a 300 watt xenon arc lamp. Light from the lamp was passed through a copper sulfate solution to remove infrared, a neutral density glass filter to regulate irradiance, a shutter assembly, and the sample. Sample optical density was determined using a tungston lamp, a bandpass filter and a silicon detector mounted on a separate optical bench positioned at an angle to the first. The photochromic response of the sample was defined as the change in optical density (ΔOD) upon exposure to the light from the xenon lamp as measured through the bandpass filter. The change in optical density was determined as a function of time of exposure and both an initial rate of change, calculated from a 30 second reading, and the equlibrium or steady state response were determined for each sample. After achieving the steady state condition, exposure to the activating radiation was discontinued and the rate of fade was measured. The fade rate was defined as the time in seconds required for the sample to return to a ΔOD of one-half the equlibrium value.

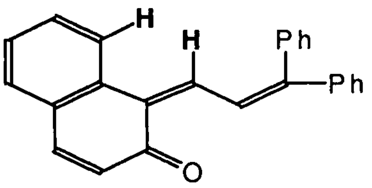
RESULTS AND DISCUSSION

As a starting point, naphthopyrans IIa and IIIa (Ar = Phenyl) were prepared from 1,1-diphenyl-2-propyn-1-ol and (respectively) β-naphthol or α-naphthol. Their photochromic properties in polymer prepared from CR-39^{R} monomer are listed below. Ia (Ar = Phenyl) was not included in the study because it is not photochromic at room temperature.

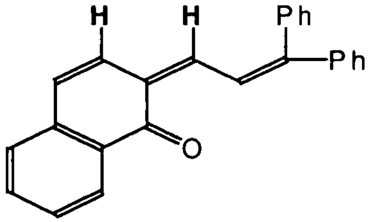
COMPOUND	ΔOD 30SEC.	ΔOD STEADY STATE	FADE T1/2 (SEC.)
IIa	0.21	0.36	45
IIIa	0.45	1.37	>1800

Compound IIa has a very good fade rate but does not achieve a very high optical density at equlibrium. On the other hand IIIa gets very dark but does not fade in a reasonable period of time. For many applications, a compound with an optical density equivalent to IIIa but with a much faster fade would be ideal. The large difference in photochromic properties between IIa and IIIa is best explained by examining the most stable open (colored) forms. These are drawn below as the quinoidal species. The actual open form may contain a considerable amount of zwiterionic character.

OPEN FORMS



IIa



IIIa

In the open form of IIa there is steric crowding of the two hydrogens highlighted whereas no such crowding exists in IIIa. The net result is that IIa returns to its colorless closed form (fades) much more rapidly than IIIa.

Substituent effects on the aryl groupings of II have been studied in some detail[13]. Electron donating groups such as methoxy in the para position(s) result in a bathochromic shift in the visible spectra as shown below.

Aryl Substituent in II	λmax (Visible)	ΔOD Steady State	Fade T1/2 (sec.)
none	432nm	0.36	45
p-MeO	468nm	0.25	35
p-MeO, p'-MeO	480nm	0.15	40

Although one methoxy has a dramatic effect on the color (36nm), one more methoxy on the second aryl group provides only an additional 12nm bathochromic shift. A secondary effect of the addition of electron donating groups is the loss in optical density at equilibrium. Next, the influence of substituents at other positions on the aryls was studied with particular emphasis being placed on ortho groupings.

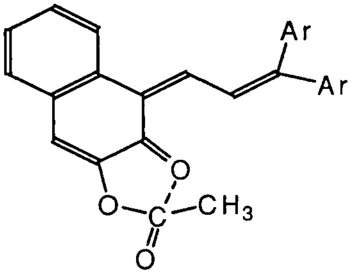
Aryl Substituent in II	λmax (Visible)	ΔOD Steady State	Fade T1/2 (sec.)
o-F, p'-MeO	456nm	1.00	170
o-F, m',p'-diMeO	472nm	1.05	203
o-Me, p,p'-diMeO	475nm	1.36	510
o-Me, p'-MeO	469nm	2.40	>600
o,p-diMeO	455nm	1.42	510
o,o-diF, p'-MeO	450nm	2.23	>1800

The above data shows that an ortho substituent dramatically slows the fade and increases the optical density. A single fluoro gives a faster fade than a single methyl or methoxy, and two ortho substituents on the same aryl group (2,6-disubstituted) results in an even slower fade. Because the electronic character of the ortho position is very similar to the para position where substitution does not result in a slowing of the fade, this effect is believed to be at least partially steric in nature.

Substitution on the naphthylene portion of the naphthopyran has also been explored[14]. The 5-methoxy and 5-acetoxy derivatives were prepared by reacting 1,1-diphenyl-2-propyn-1-ol with 3-methoxy-2-naphthol and 3-acetoxy-2-naphthol.

5-Substituent in II	λmax (Visible)	ΔOD Steady State	Fade T1/2 (sec.)
none (control)	432nm	0.36	45
methoxy	432nm	0.46	120
acetoxy	455nm	0.44	81

Whereas methoxy substitution on the aryl group(s) of II resulted in a bathochromic shift for the colored species along with a loss in optical density, a methoxy on the naphthylene had no influence on the color, slowed the fade and increased the equilibrium optical density somewhat. An acetoxy group (electron withdrawing) at the same position has a very unexpected effect. In view of the fact that electron withdrawing groups on the chromophore would be expected to result in a hypsochromic shift in the color, just the opposite is observed with a bathochromic shift of 23nm. A possible explanation of this anomaly is that the open (colored) form of this photochromic naphthopyran may have the quinoidal oxygen coordinated to the carbonyl carbon of the acetoxy group. Note that a similar structure can also be drawn for the zwiterionic species.



This would have the overall effect of lengthening the chromophore resulting in absorption at longer wavelengths.

CONCLUSION

Substituents on 3,3-phenyl-3H-naphtho [2,1-b]pyrans have been found which dramatically change photochromic properties versus the unsubstituted parent. Ortho groups on the aryls give compounds of high optical density and reasonable fade. The color of the open form can be shifted from yellow to orange by the addition of electron donating groups to the para position(s) of the aryls and/or by substituting an acetoxy group at the 5-position on the naphthalene portion of the molecule.

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