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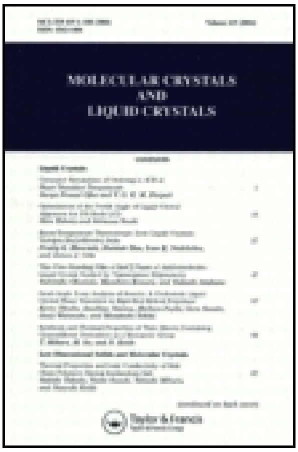

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Naphthopyrans. Structural Features and Photochromic Properties

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NAPHTHOPYRANS. STRUCTURAL FEATURES AND PHOTOCHROMIC PROPERTIES

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Abstract Structural modifications to photochromic 3H-naphtho[2,1-b]pyrans and 2H-naphtho[1,2-b]pyrans have produced compounds that have found utility in plastic ophthalmic lens applications. The influence of substituents on color, optical density, and fade rate are reported. Synthetic routes to products and key intermediates are also outlined.

INTRODUCTION

Ten to twenty eight years ago Becker, in a series of papers[1], reported on the photochromism of benzopyrans (chromenes) and naphthopyrans. Although Heller[2,3] prepared some naphthopyran derivatives in the mid 1980's, further studies on this class of compounds did not occur until the late 1980's and early 1990's when commercial sales of photochromic plastic ophthalmic lenses served as the spark for renewed interest in this class of compounds. Photochromic naphthopyrans, which are yellow to red in the activated (colored) state, can be divided into two sub groups: the 3H-naphtho[2,1-b]pyrans and the 2H-naphtho[1,2-b]pyrans (Figure 1, **A** and **B** below, respectively.)

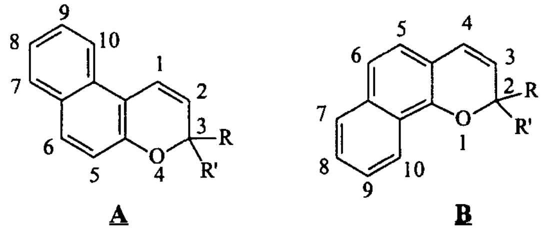

FIGURE 1 Naphthopyrans, structure and numbering system.

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With similar substitution at the R and R' positions, **A** will be much less intense and fade much faster than **B**. To explain these observations it is necessary to examine the open form(s) of the isomeric naphthopyrans. Results from an experiment by Becker[4] in which he isolated a chemically reduced product derived from the open form, suggests that the colored species derives from the breaking of the carbon-oxygen bond of the pyran.

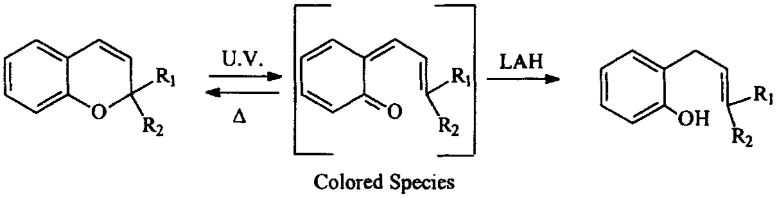

FIGURE 2 Becker's "proof of structure" of the open form.

The experiment did not determine if the colored species is quinoidal (as drawn above) or alternatively possesses radical or zwitterionic characteristics. Recently Crano[5] has reported that a low temperature NMR study of 3,3-diphenyl-3H-naphtho[2,1-b]pyran shows the spectrum of the open form to be most consistent with a quinoidal structure. The quinoidal open forms of 3H-naphtho[2,1-b]pyran and 2H-naphtho[1,2-b]pyran are compared in Figure 3.

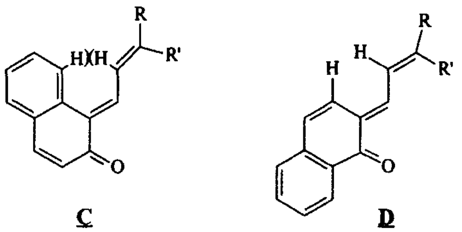

Figure 3 Open forms of 3H-naphtho[2,1-b], and 2H-naphtho[1,2-b]pyrans.

In **C** there is severe steric crowding resulting in a destabilization of the open form and rapid conversion (fading) to the closed form. No such crowding exists for **D**

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and the open form is therefore more stable and slower to convert (fade) to the colorless ground state.

For naphthopyrans to be considered for commercial use in plastic ophthalmic lenses, they must possess a reasonable level of fatigue resistance. Padwa[6] demonstrated (in work that in all likelihood can be applied to naphthopyrans) that benzopyrans, substituted at the carbon next to the pyran oxygen with a group containing an α-hydrogen, will undergo an irreversible 1-7 sigmatropic hydrogen shift.

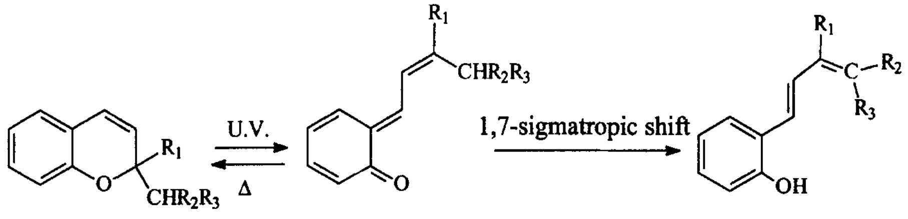

Figure 4 A major fatigue pathway for benzo (and naphtho) pyrans.

Appropriately substituted naphthopyrans that are incapable of undergoing this 1,7-sigmatropic hydrogen shift apparently have sufficient fatigue resistance to be used commercially. It has recently been reported[7] that all plastic photochromic ophthalmic lenses currently being marketed contain at least one naphthopyran.

3H-NAPHTHO[2,1-b]PYRANS

For compounds of general structure **A** to have any reasonable level of photochromism, R and R' need to be conjugative substituents such as phenyl. The aryl groupings of 3,3-diaryl-3H-naphtho[2,1-b]pyrans can be further modified for example with ortho substitution[8] to enhance their steady state optical density. This increase in optical density can be attributed to a slowing of the fade of the colored species.

Substitution on the naphtho-portion of **A** can also alter the photochromic properties of the molecule. Compare, for example the effect of methoxy

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substitution, at positions 5 through 9.[9,10] Note that the 10-methoxy compound has not been reported in the literature. Table I reports the effect on both the visible and UV absorption spectra. The visible (activated) color is obviously important for tailoring mixtures of photochromics to achieve desirable colors, for example grays and browns. The most important factor in determining activity under solar illumination is the compound's ultraviolet absorption. Short wavelength UV is attenuated by the atmosphere to a greater extent than long wavelength UV. Photochromics that absorb (activate) at shorter wavelengths will be less responsive not only early and late in the day and at higher latitudes but also in winter months when the sun is at lower angles and its rays must travel a greater distance through the atmosphere to reach the surface of the earth.

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TABLE I 3,3-Diphenyl-3H-naphtho[2,1-b]pyrans: effect of methoxy substituents.

Position	λMax (Vis.,Open Form)	λMax (UV, Closed Form)
(control, unsubstiuted)	432 nm	359 nm
5	432 nm	323 nm
6	440 nm	370 nm
7	432 nm	365 nm
8	473 nm	376 nm
9	429 nm	326 nm

As can be seen from Table I, methoxy substitution at the 6- and 8-positions provide the greatest enhancement (bathochromic shift) to the ultraviolet absorption spectrum of the closed form. A methoxy at the 8-position produces a bathochromic shift in the visible of 41nm, while substitution at all other positions have little effect on the absorption of the colored species. Other electron donating groups, such as amino, have been shown to have similar effects.[11,12]

3,3-diaryl-3H-naphtho[2,1-b]pyrans are most conveniently prepared in the two step process outlined in Figure 5. In the first step, a substituted or unsubstituted benzophenone is reacted with sodium acetylide to produce a 1,1-diaryl-2-

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propyn-1-ol. In the second step, this intermediate is condensed under acidic conditions with a substituted or unsubstituted 2-naphthol to produce the pyran.

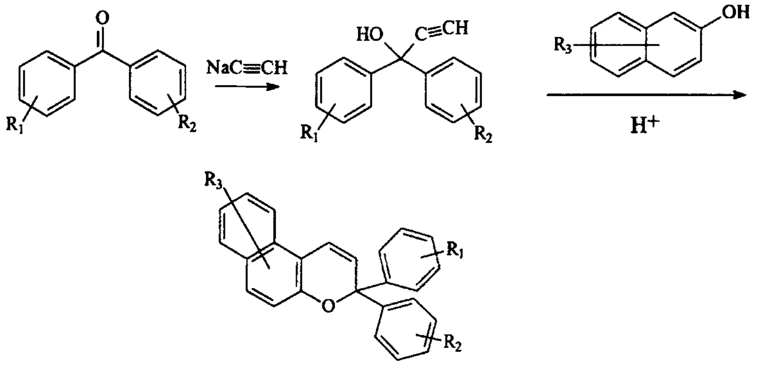

FIGURE 5 Synthesis of 3,3-diaryl-3H-naphtho[2,1-b]pyrans.

2H-NAPHTHO[1,2-b]PYRANS

Naphthopyran **B** with R and R' combined to form a polycyclic aliphatic group, for example adamantane[2] or bicyclononane[13] produce intense yellow photochromics with a reasonable level of fade. These derivatives are best prepared via the Kabbe reaction[14] as shown in Figure 6.

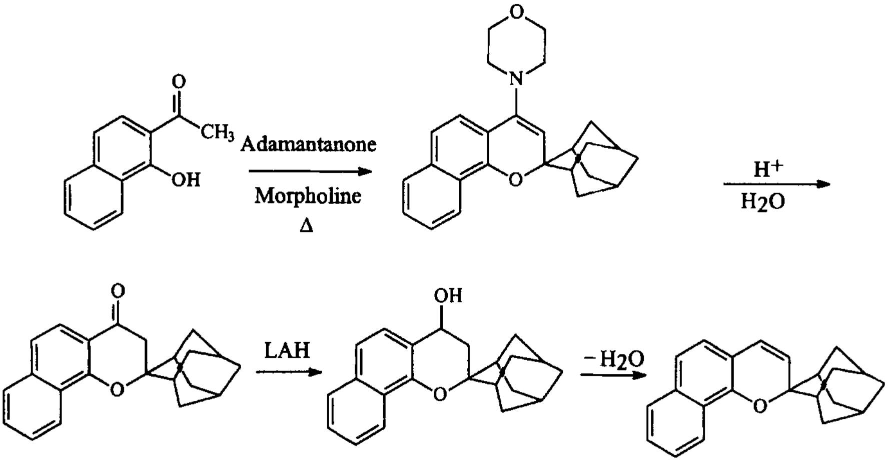

FIGURE 6 Synthesis of 2-spiroadamantylidene-2H-Naphtho[1,2-b]pyran.

When R and R' are aryl, the compounds are far too slow to fade for use in optical plastics. Examining the open form of naphthopyran **B**, (**D**, Figure 3) it is obvious that substitution at the 5-position should result in a destabilization (increasing the rate of fade) due to steric crowding (as is observed in the open form **C** of naphthopyran **A**). The effect of 5-substitution is shown in Table II.

TABLE II 2,2-Diphenyl-2H-naphtho[1,2-b]pyrans: effect of 5-substitution on fade.

5-Substituent	6-Substituent	Fade T1/2 in Optical Plastic
Hydrogen	Hydrogen	>1800 Seconds
Methyl	Hydrogen	640 Seconds
Carbomethoxy	Hydrogen	54 Seconds
Carbomethoxy	Methyl	717 Seconds

These data show that carbomethoxy[15] is a much more effective promoter of fade than methyl. This can be explained by considering that π-overlap between the carbomethoxy substituent and the naphthalene (Figure 7) encourages the substituent to lie coplanar where its bulk is most effective.

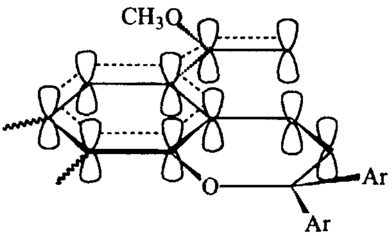

FIGURE 7 π-Overlap between carbomethoxy and naphthalene.

Groups such as methyl, that can freely rotate out of the plain, are less effective. A 6-substituent such as methyl will cause the 5-carbomethoxy substituent to be pushed out of coplanarity resulting in its effectiveness as a fade promoter becoming roughly equivalent to that of methyl.

Fade rates and colors of 2,2-diaryl-2H-naphtho[1,2-b]pyrans in optical plastics can be further adjusted with appropriate substitution as shown in Table III. Electron donating groups such as methoxy when substituted at the para

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TABLE III 2,2-Diaryl-5-carbomethoxy-2H-naphtho[1,2-b]pyrans: effect of substituents.

6-Substituent	Diaryl Groups	Fade T1/2	λMax Visible
Methyl	Phenyl	717 Seconds	475 nm
Methyl	p-Methoxyphenyl	217 Seconds	505 nm
Methoxy	p-Methoxyphenyl	305 Seconds	510 nm
Acetoxy	p-Methoxyphenyl	74 Seconds	509 nm

positions of the diaryl groups or at the 6-position of the naphthalene results in the visible spectrum being shifted bathochromically. Fade rates will be enhanced with alkoxy substitution on the 2,2-diaryl groups but conversely will be retarded when alkoxy is substituted at the 6-position. Acetoxy substitution at the 6-position enhances fade and red shifts the visible absorption. 3-Carbomethoxy-1-naphthols (starting materials for 2,2-diaryl-5-carbomethoxy-2H-naphtho[1,2-b]pyrans) are conveniently prepared as outlined in Figure 8.

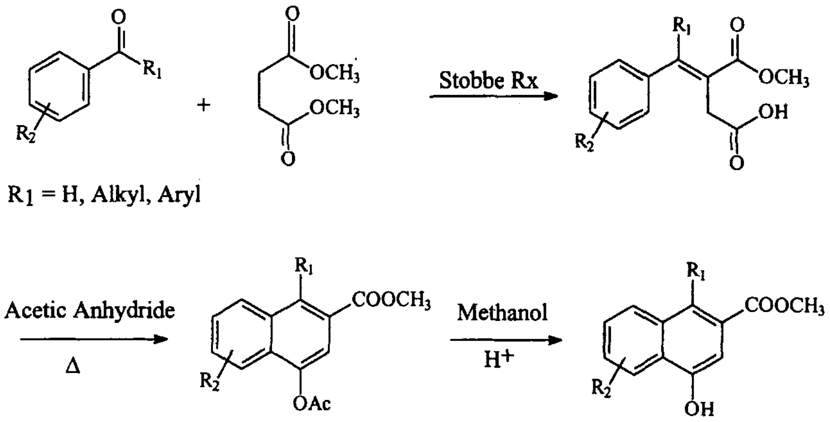

FIGURE 8 Synthesis of 3-carbomethoxy-1-naphthols.

Once the naphthol is prepared it can be condensed with a propargyl alcohol as described previously for the 3,3-diaryl-3H-naphtho[2,1-b]pyrans (see Figure 5).

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CONCLUSIONS

Substitution to both the 3H-naphtho[2,1-b]pyrans and the 2H-naphtho[1,2-b]pyrans have produced photochromic compounds with good colorability and a wide range of fade rates. These compounds are yellow to red in the activated state. Photostability (resistance to fatigue) is high enough that these compounds have found use in plastic ophthalmic lenses.

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