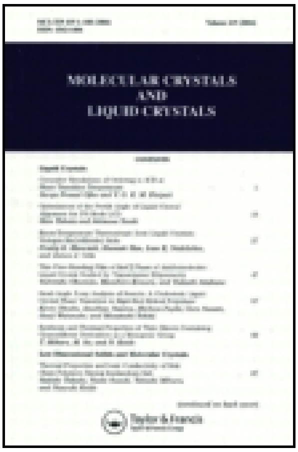

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THE EFFECT OF SUBSTITUENTS ON THE RING CLOSURE REACTION OF PHOTO ACTIVATED DIARYLNAPHTHOPYRANS

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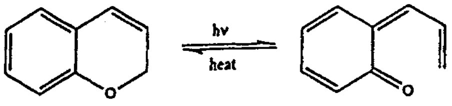
Abstract A kinetic study of a few photochromic diarylnaphthopyrans is reported. Upon exposure to ultraviolet radiation, the diarylnaphthopyran derivatives are transformed into open chain, colored forms, which undergo ring closure into the colorless pyran forms. The rate of the ring closure has been determined for a few diarylnaphthopyrans. The effect of substituents on this reaction is briefly investigated.

2-H-Chromene (I) and its derivative have been known to be photochromic since the work of Becker in the mid 1960's[1].

Photochromic substances are compounds that undergo a reversible transformation upon exposure to ultraviolet (UV) radiation. The product of this photochemical rearrangement absorbs visible radiation and exhibits color. The conversion of the colored to the non-colored form is catalyzed by heat and/or visible light. This cycle may be repeated a number of times until the phenomenon of photo degradation (i.e. light fatigue) occurs. At this point, the material loses the ability to exhibit photochromic behavior[2]. Becker proposed the following equilibrium to account for the photochromic activity of chromene:

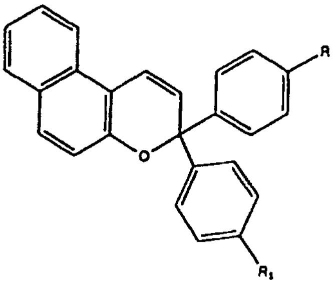


II

SCHEME 1

Structure II corresponds to the colored form.

In U.S. Patent 5,006,818 Van Gemert[3] describes the synthesis of certain photochromic diarylnaphthopyrans that possess a high quantum efficiency for the photo coloration reaction in the near ultraviolet region. He also states that substituents at the meta and para positions of compounds such as 3,3 - diphenyl - 3H - naphtho [2,1-b] pyran (III) will increase the rate of the ring closure reaction.



III

However, the introduction of an ortho substituent on an aryl group with or without the presence of meta and/or para substituents, will retard the rate of the ring closure reaction. 2-6 - Disubstitution on the same aryl group results in an even slower ring closure reaction. VanGemert has stated that because the ortho position is electronically similar to the para position, this effect is probably due to steric interactions. It was also discovered that election donating groups in the para position result in a bathochromic shift in the visible absorption spectrum of the open form.

Continuing the study of the diarylnaphthopyrans, this paper presents results in an attempt to learn more about the rate of thermal reversion of the diarylnaphthopyrans. Another goal is to evaluate the influence of substituents in the aryl rings on the kinetics of the ring closure reaction.

MATERIALS AND METHODS

The materials in question were synthesized by an acid catalyzed condensation between a naphthol and a 1,1-diaryl-2-propyn-1-ol.[4] Photochromic properties were measured at 22°C. Photochromic naphthopyrans were prepared by the acid catalyzed reaction of naphthol with diaryl propargyl alcohols. In general they were purified by column chromatography and crystallization. For testing purposes the compounds were imbibed into polymer CR.-39^{R}. Properties were measured on an apparatus utilizing an Ealing Triangular optical bench equipped with 300 watt xenon arc lamp. Light from the lamp was passed through a copper sulfate solution to remove infrared radiation, a neutral density glass filter to regulate irradiance, a shutter assembly, and the sample. Sample optical density was determined using a tungsten 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 at both an initial rate of change, calculated from a 30 second reading, and the equilibrium or steady state response 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 is defined as -d[MC]/dt where [MC] = the concentration of the colored merocyanine form. The half life (T 1/2) is defined as the time in seconds required for the sample to return to a ΔOD of one-half the equilibrium value.

RESULTS AND DISCUSSIONS

The thermal decay of a typical diarylnaphthopyran (DANP) is shown in Figure 1. ΔOD (which corresponds to absorbency) is proportional to [MC] according to the Beer Lambert Law:

$$\varepsilon = \frac{A}{CL} \tag{1}$$

where = molar absorptivity
A = absorbency
C = concentration, in M
L = cell length, in cm

The rate of thermal reversion at any particular point was determined by drawing a tangent to the curve and calculating its slope. Time, ΔOD, and rate data for the thermal fade of the DANP are shown in Table I.

TABLE I Ratio of DANP thermal reversion @ 72 degree F

Time(s)	60	90	120	181	241	301
ΔOD	0.298	0.221	0.171	0.117	0.092	0.078
Rate(mol/L•S)	3.1E-3	2.0E-3	1.2E-3	5.9E-4	2.4E-4	1.6E-4

A plot of rate vs. ΔOD is shown in Figure 2.

For all times less than 160 seconds, the plot of rate vs. ΔOD is a straight line, which is indicative of a first-order reaction.

Utilizing compiled $t_{1/2}$ data and the following equation for the half-life of a first order reaction:

$$T_{1/2} = \frac{0.693}{k} \tag{2}$$

Thermal reversion rate constants for various para-substituted DANPs were calculated. The data is shown in Table 2 along with the substituent constant, σ for para-substituted DANPs of the following form.

TABLE II Rate constants for the thermal reversion of various DANPs & σ values

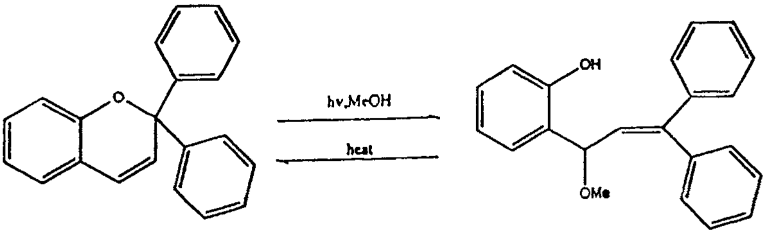
	R	R	k	σ
III	-H	-H	1.925E-2	
IV	-H	-OMe	1.98E-2	-0.27
V	$-CH_3$	-H	2.31OE-2	-0.17

Allowing the thermal reversion of III to serve as the reference reaction (k_o) and utilizing the Hammett equation[5]

$$\log k - \log k_o = \rho\sigma \qquad (3)$$

One may calculate the reaction constant (ρ). The magnitude of the rho value indicates the sensitivity of the reaction to substituent effect. For the thermal reversion of the DANPs, the rho values are approximately -0.016 at 25°C.

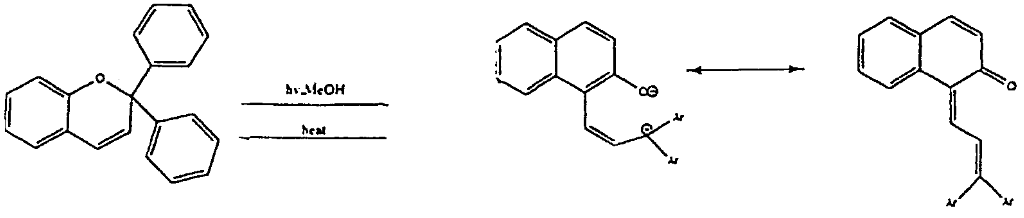
Padwa et al[6] had previously examined the photochemical ring opening of the structurally related 2,2-diphenylchromene whose photochemical behavior in methanol is depicted in Scheme 2.



SCHEME 2

Padwa explained the results by postulating that a photochemical ring opening occurs which yields an o-quinoneallide intermediate. The intermediate then undergoes 1,4 addition of methanol to yield an unstable photo adduct that reverts to III upon standing in the dark. The formation of the postulated quionone-like intermediate is consistent with Becker's discoveries[7].

If the photochemical ring opening and thermal ring closure reaction involved a zwitterionic structure,



SCHEME 3

the presence of electron donating groups in the para-position on the aryl groups would tend to stabilize the positive charge on the benzylic carbon of the zwitterionic form. This would stabilize the MC relative to the unactivated DANP and decrease the rate of thermal reversion. However, this does not occur in the case of the DANPs. This appears to indicate that the zwitterionic form of the MC form of the DANPs is minutely involved, if at all, in the thermal reversion reaction. This statement is in agreement with Becker's concerted electrocyclic thermal reversion mechanism.

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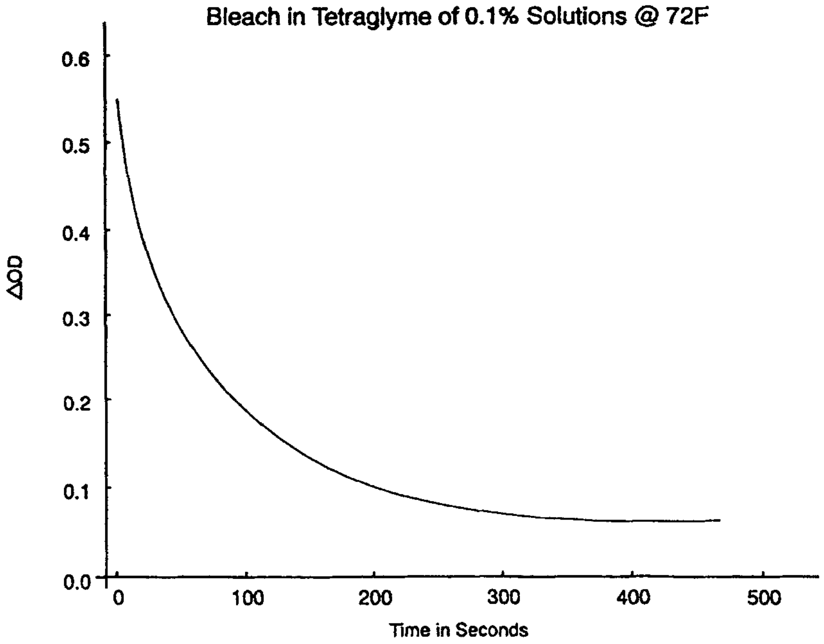

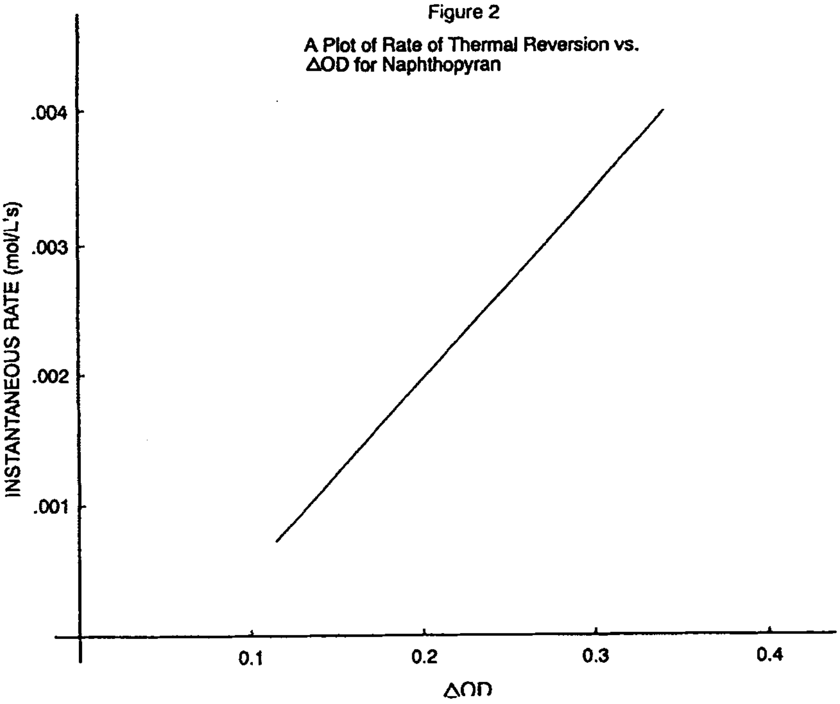
Figure 2

A Plot of Rate of Thermal Reversion vs. ΔOD for Naphthopyran