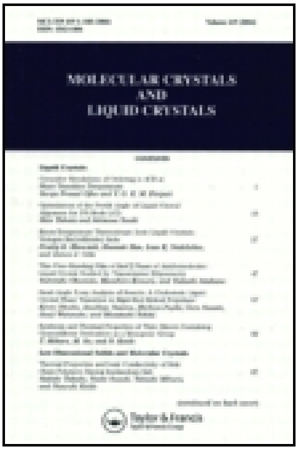

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A NEW PHOTO/THERMOCHROMIC SOLID COMPOUND OF THE INDENONE OXIDE FAMILY.

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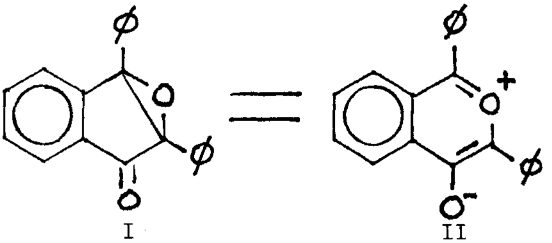
Abstract: A new strong photochromic solid compound, a 3-ketone of the 2,3-diphenylindenone oxide, has been prepared for first time. The new compound exhibits very strong photochromic and thermochromic phenomena.

INTRODUCTION

Researchers[1] have examined the photochromic behaviour of 2,3-diphenylindenone oxide (I) in order to study the geometric and energetic changes which occur during the primary photochemical processes and have shown that I and its valence tautomer II can be photochemically interconverted and they suggested that, in a condensed phase at room temperature, both the forward and reverse reactions proceed via vibrationally excited ground states of the two tautomers. However our variable temperature flash photolysis study of 2,3-diphenylindenone oxide (I), 2,3-diphenyl-4,



(1)

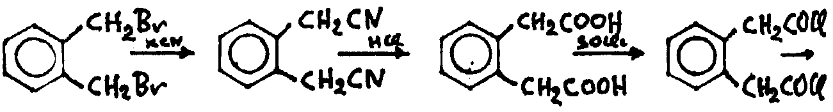
7-dimethylindenone oxide (III) and tetraphenyl-2,3-diphenylindenone oxide (IV) showed the existence of two transients which contribute to the photochemical valence tautomerization of these compounds[2].

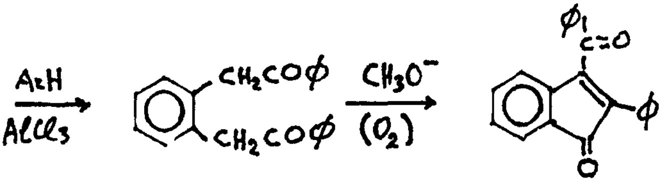
Solid I turns red when irradiated but nothing has been reported about the termo- or photochemistry of the solid state coloration[3]. Therefore we decided to examine further the solid compounds I,III and IV and, also, to prepare 3-ketones of this family of compounds. These have not been prepared or investigated till now but have been suggested as possible interesting photochromic materials[4]. In this paper, among other matters, the first successful preparation of a 3-ketone of the 2,3-diphenylindenone oxide with very strong photochromic and thermochromic properties is reported.

EXPERIMENTAL

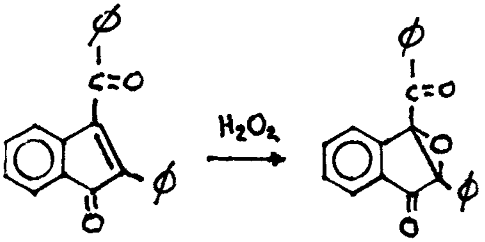
2,3-Diphenylindenone oxide (I) was prepared according to literature[5] and was recrystallized from ethanol-water to a constant melting point of 142-143°C. 2,3 Diphenyl-4,7--dimethylindenone oxide (III), and tetraphenyl-2,3-diphenylindenone oxide (IV) were also prepared by this method and had melting points of 98°C and 198°C respectively.

The new 3-ketone compound was prepared according to the sequence of the following known reactions[6].





The epoxidation of the last compound leads to the 3-ketone (V).



(V)

The new compound V has m.p.= $166^{\circ}C$ and its purity was verified by stoichiometric analysis and i.r. spectra.

The photochromic and **thermochromic** properties were tested in powders of the compounds and in polycrystalline thin films prepared between quartz optical glasses by melting and slow cooling under pressure.

A 200W H.B.O. high-pressure mercury lamp **with** appriate filters was used for the irradiations.

The thin polycrystalline films were irradiated under stable temperature with the help of a thermostated cell adaptor. For measurements at lower temperatures a special Dewar flask with optical quartz windows was used in connection with liquid nitrogen and a thermocouple.

RESULTS AND DISCUSSION

Irradiation with light of 365 nm of a thin polycrystalline film of 2,3-diphenylindenone oxide (I) results in the formation of a coloured form, the benzopyrylium oxide II, which shows a maximum absorption around 530 nm. This form on standing in the dark reverts back in the form I.

The formation of II for various times of irradiation is shown in Figure 1a while in Figure 1b we follow the thermally reversible change of II to I.

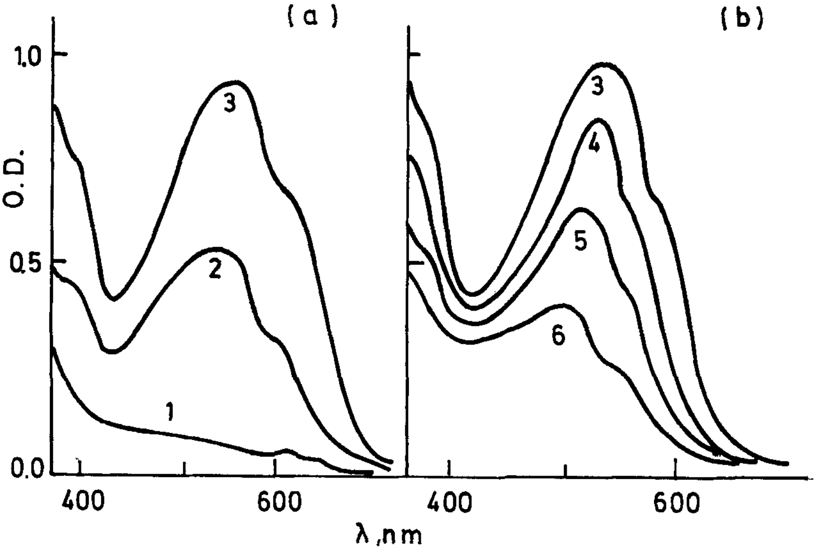


FIGURE 1. (a) Absorption spectra of a polycrystalline thin film of 2,3-diphenylindenone oxide (I) at RT. 1 : before irradiation 2 : after 2 hrs irradiation 3 : after 3 hrs irradiation (photoequilibrium).

(b) Absorption spectra of a polycrystalline thin film of 2,3-diphenylindenone oxide at RT after the photoequilibrium (3). 4 : after 1 hr in the dark 5 : after 4 hrs in the dark 6 : after 7hrs in the dark.

After standing in the dark for 2 to 3 days, the absorption spectrum is almost identical to the starting one (before irradiation). The results are better when the irradiation is performed at low temperatures since then the production of side products is kept minimal and the crystallinity of the film is protected.

We have more or less similar results on irradiation of thin polycrystalline films of 2,3-diphenyl-4,7-dimethylindenone oxide (II) at room temperature and at liquid nitrogen temperature.

KINETICS

A polycrystalline thin film of the compound I which has been irradiated with light of 365 nm. contains a great number of molecules of II (photo-product). These molecules convert in the dark back to form I with a first order rate constant according to the equation:

$$\mathrm{I} \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \mathrm{II} \qquad (2)$$

This rate constant K_{-1} can be calculated if we make two assumptions: 1) we assume that important side reactions do not exist and 2) $K_1 \ll K_{-1}$. The first assumption is usually satisfied in the solid state. At equilibrium the proportion of molecules II in the crystalline thin film is very small as is seen from the absorption spectrum of figure 1 (curve 1) and therefore $K_{eq} \ll 1$.

With these two assumptions and equation 2 we can write:

$$\frac{d\,\{II\}}{dt} = K_1\,\{I\} - K_{-1}\,\{II\} \qquad (3)$$

$$\{I\}_o = \{I\} + \{II\} \qquad (4)$$

where $\{I\}$ and $\{II\}$ are considered to be the "concentrations" or the proportions of molecules I and II in the polycrystalline thin film at each moment and $\{I\}_o$ is the initial "concentration" of I before irradiation.

Equation 3 is transformed to 5 :

$$-\frac{d\,\{II\}}{dt} = (K_1 + K_{-1})\,\{II\} - K_1\,\{I\}_o \qquad (5)$$

which on integration gives :

$$\ln \frac{(K_1+K_{-1})\,\{II\}_m - K_{-1}\{I\}_o}{(K_1+K_{-1})\,\{II\} - K_{-1}\,\{I\}_o} = (K_1+K_{-1})\,t \qquad (6)$$

where $\{II\}_m$ is $\{II\}$ for $t = 0$ (maximum).
In the state of equilibrium ($t = \infty$) equation 5 becomes:

$$0 = (K_1 + K_{-1})\,\{II\}_{eq} - K_1\{I\}_o \qquad (7)$$

where $\{II\}_{eq}$ is the $\{II\}$ for $t = \infty$ (equilibrium).
Replacement of $\{I\}_o$ from 7 to 6 results in 8 :

$$\ln \frac{\{II\}_m - \{II\}_{eq}}{\{II\} - \{II\}_{eq}} = (K_1 + K_{-1})\,t \qquad (8)$$

Considering the optical densities (O.D.) to be proportional to the concentrations and remembering our second assumption ($K_1 << K_{-1}$) we end with the equation 9.

$$\ln \frac{(O.D)_m - (O.D)_{eq}}{(O.D) - (O.D)_{eq}} = K_{-1}t \qquad (9)$$

Therefore a graph of the first part of this equation versus time (t) results in a straight line the slope of which is K_{-1}. The rate measurement at various temperatures is shown in Figure 2a. Finally, using the Arrhenius equation, plotting log K_{-1} versus 1/T (Figure 2b) we find the energy of activation of the reverse reaction II $\xrightarrow{K_{-1}}$ I which for the case under examination is $E_\alpha \approx 14$ Kcal/mole.

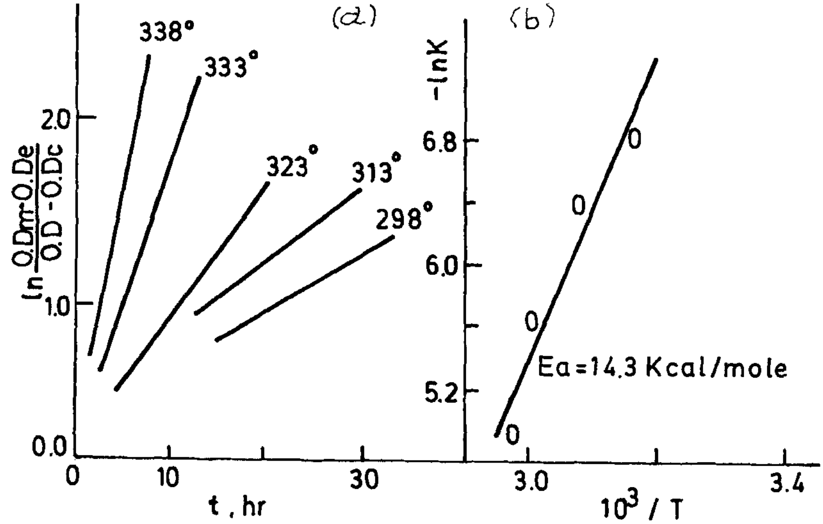


FIGURE 2 : (a) Graphic representation of the first-order reversible process of the photo-product II to I at various temperatures in the solid state.

(b) Arrhenius plot of the first-order reversible process of the photo-product II to I in the solid state.

THE NEW PHOTO/THERMOCHROMIC COMPOUND

The newly prepared compound, a 3-ketone (V) of indenone oxide (I), presents a special feature : it bears a carbonyl group near the reaction center. Since carbonyl groups are in general very reactive towards light, some kind of interaction is expected between this group and the reaction center upon breaking the three-membered ring. Differences from the generally accepted mechanism[2] because of the presence of the carbonyl group is under investigation.

However, the compound presents very strong photochromism in the solid state. It turns from white to red reversibly. A detailed photochemical and photophysical investigation of this compound is under way.

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