

## Dihetarylethene photocyclization as a synthetic route to fluorescent compounds



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### ABSTRACT

It was shown that UV irradiation of imidazoline-bridged dihetarylethenes affords fused products exhibiting fluorescence. The starting compounds were prepared by three-component condensation of *N,N'*-dimethylurea with arylglyoxals and enols. A method was proposed for the synthesis of polycyclic imidazole derivatives by photoinduced cyclization followed by elimination of a water molecule. The advantages of the method include readily accessible starting compounds, process simplicity, and the ease of isolation of the target products. The crystal structure of the cyclization products was determined. It was shown that unlike the starting imidazol-2-ones, all photochemically prepared polycyclic products exhibit intense fluorescence.

### 1. Introduction

The improvement of information technologies plays an important role in the development of a global community. A need for increasing the capacity of data storage media and the speed of data processing entails the development of the next-generation optical data storage technologies. In this connection, the change of modern one-photon Blu-ray optical disks with information capacity of 25 GB by two-photon 3D optical disks with information capacity more 1 TB is of great importance [1]. The essence of this nonlinear optical process is the simultaneous absorption of two lower-energy photons, which are not absorbed by a light-sensitive system upon one-photon excitation. The two-photon transformation of light-sensitive substances occurs in each layer of the multilayer recording media only at a particular threshold power density of activating radiation in any specified region of the bulk recording medium and provides high resolution. Light – sensitive recording media providing non-destructive fluorescence readout of optical data have attracted great interest [2].

The development of light-sensitive recording media for archival 3D optical disks is based on the use of irreversible photochemical transformations of non-luminescent organic compounds into fluorescent

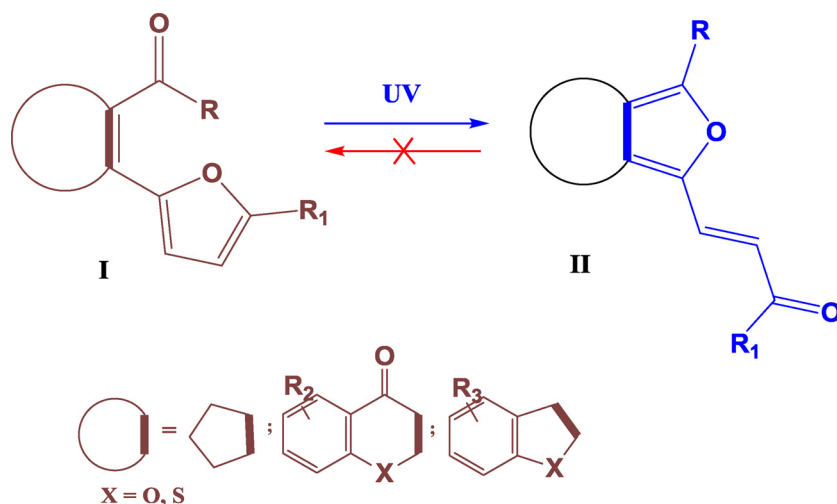
photoproducts [2]. Most often the photochemical transformation of colorless leu-co compounds into colored fluorescent dyes in the presence of acid generators providing a photoinduced pH change are used for this goal [3–6]. Such recording media are suitable for the fabrication of optical disks with data storage capacity of 1 Tb and the data recording speed up to 1GB/s. However, since most of the above-considered photofluorescent compounds and systems have small Stokes shifts, they are of little use in 3D optical memory.

In this regard we have suggested to use as light-sensitive substances chromones, forming fluorescing photoproducts with more acceptable Stokes shift [7–10]. Previously, we have shown that chromones and structurally related compounds **I** with a 3-furan-2-ylpropene moiety, which do not exhibit fluorescence, are converted to fluorescent products **II** on exposure to ultraviolet light (Scheme 1).

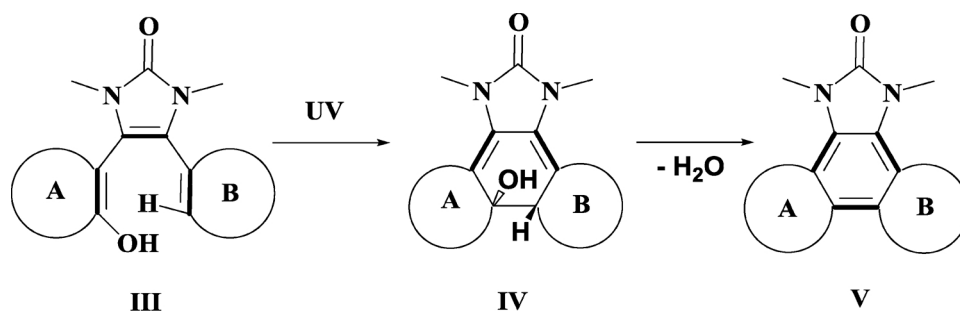
Compounds with this type of properties could find use for the design of recording media for optical storage devices [11–14].

Our further search for compounds that generate fluorescent products on exposure to ultraviolet radiation resulted in imidazole derivatives **III**, which undergo photoinduced 6 $\pi$ -electrocyclization to afford compounds **IV**. The latter spontaneously eliminate water, being converted to products **V** (Scheme 2).

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Scheme 1. Photocyclization of chromones and their structural analogues.



A, B = aromatic / heteroaromatic ring

Scheme 2. Photocyclization of diarylethenes.

The purpose of the present study is to obtain the initial imidazol-2-ones **III** and their photoproduct prepared by long exposure to UV light, identify the fused cyclization products as well as to investigate absorption and fluorescent properties of the initial compounds and their photoproducts.

## 2. Results and discussion

### 2.1. Synthesis

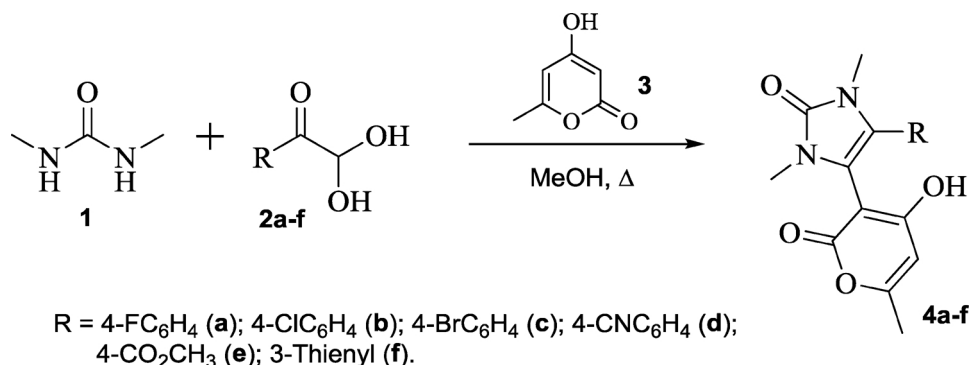
The starting imidazol-2-ones **4** were prepared by a reported procedure [15] via the condensation *N,N*-dimethylurea with arylglyoxals and enols. 4-Hydroxy-6-methyl-2H-pyran-2-one **3** was used as the enol component, which resulted in the formation of derivatives **4** in 25–64%

yields (Scheme 3).

This reaction can be performed for a fairly broad range of arylglyoxals with different types of substitution. In order to rule out the formation of regioisomer mixtures, arylglyoxals containing chemically equivalent protons in the *ortho*-positions relative to the carbonyl group were chosen for the photocyclization.

Ultraviolet irradiation (365 nm) of dihetarylethenes **4** was carried out at room temperature for 6–15 h. Because of low solubility of these compounds, reasonable concentrations ( $10^{-2}$  M) were attained only with *N*-methyl-2-pyrrolidone being used as the solvent.

In all cases, the formation of fused photoproducts was detected. The photochemical reaction was monitored by means of  $^1\text{H}$  NMR spectroscopy. As an example, Fig. 1 presents the results of irradiation of compound **4b** (0.015 mmol) in  $\text{DMSO-}d_6$  (0.7 mL) in a standard NMR

Scheme 3. Synthesis of 1,3-dimethyl-1,3-dihydro-2H-imidazol-2-ones **4**.

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