Dyes and Pigments 141 (2017) 269–276

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Grey colouring thermally reversible photochromic 1-vinylidene-naphthofurans

Céu Sousa, Sofia Saraiva, Helena Macedo, Paulo Coelho*

Centro de Química - Vila Real, Universidade de Trás-os-Montes e Alto Douro, 5001-801, Vila Real, Portugal

ARTICLE INFO

Article history:
Received 15 January 2017
Received in revised form
13 February 2017
Accepted 14 February 2017
Available online 16 February 2017

Keywords:
Naphthofuran
Silica gel
Photochromism
Ring-opening
Grey colouration
Photoswitches
UV light

ABSTRACT

A set of new 1-vinylidene-naphthofurans substituted by styryl groups were synthetized. These compounds show photochromic properties when adsorbed in silica gel, or in acidified THF solutions, developing intense colours after exposure to the UV light and returning to the uncoloured state, in the dark, in several minutes. The introduction of the styryl chain extends the conjugation of the photoproducts and shifts their absorption bathochromically relative to the parent unsubstituted naphthofuran. For styryl-naphthofuran **5a**, in an acidified THF solution, an intense grey colouration can be achieved after 1 min of UV exposure (or direct sunlight) and the decolouration, in the dark, occurs in less than 10 min at room temperature.

1. Introduction

While classic dyes exhibit a permanent colour, photochromic dyes have the ability to change their colouration through a reversible, light induced, isomerization reaction [1]. Usually, these smart molecules are uncoloured in the dark but are converted into a coloured photoisomer upon exposure to the UV light, which reverts back to the initial state, spontaneously or through irradiation with visible light. The photochemical reactions behind this phenomena commonly involve unimolecular reactions like *cis-trans* isomerization [2], electrocyclic ring opening/closing [3], heterolytic bond breaking [4], proton transfer [5] and induces a significant molecular modification, that changes not only the colour, but also the molecular volume [6], polarity [7], reactivity [8], solubility [9], etc. These photoswitchable properties have been explored in different ways in materials chemistry [10] and recently in some biological applications [11].

Thermally reversible photochromic molecules, like the naphthopyrans, spiropyrans and spiroxazines are photochemically converted into a thermally unstable coloured specie that returns spontaneously to the initial state, once the system is placed in the dark [1]. This phenomenon occurs typically in solution or when the molecules are dispersed in polymeric matrices, although their properties, in particular the switching speed, are particularly affected by the chemical environment surrounding the photosensitive molecule [12]. The possibility to reversibly change the colour of a lightweight material using only the sunlight attracted the industry attention that explored their application in lenses [13], windows [14] and textiles [15]. By far, the most developed technology, using these smart dyes, are the photochromic ophthalmic lens that darken under sunlight exposure. However, although a vast number of photochromic dyes have been reported and patented, few have been commercialized due to the long list of requirements that the development of a marketable product imposes [16]. The photoactive molecule must be easy and economical to synthesize, soluble in the media, uncoloured in the dark, exhibit a fast colouration under sunlight, provide an intense colouration with the require shade (grey or brown) using a low concentration of the dye, exhibit a high fading rate while not compromising a high concentration of the coloured species since these aspects tend to be mutually exclusive, show a low dependence with temperature and resist to photodegradation allowing to execute many colouration/decolouration cycles without losing their performance. Some naphthopyrans meet almost all of these requirements, but in order to reach intense colourations the industry uses compounds that

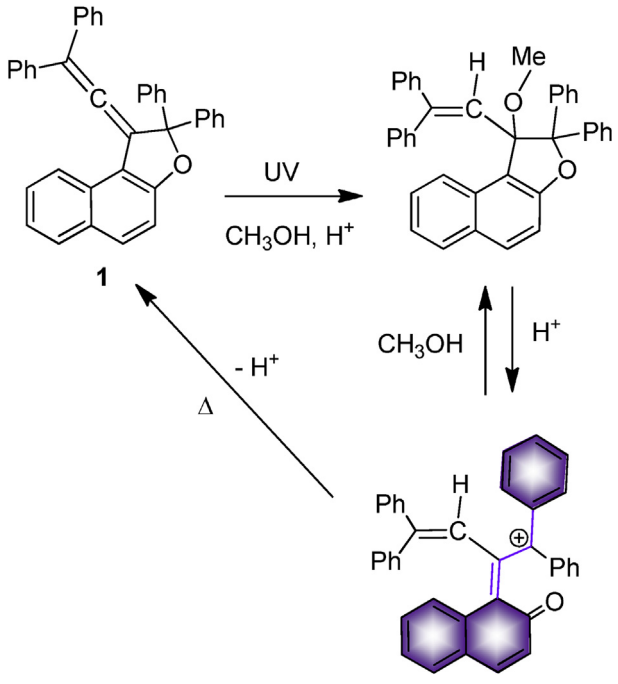
* Corresponding author.
E-mail address: pcoelho@utad.pt (P. Coelho).

http://dx.doi.org/10.1016/j.dyepig.2017.02.027
0143-7208/

generate undesirable long-lived coloured photoisomers. In fact, although the commercial photochromic lenses are quickly activated by sunlight (<30 s), they exhibit a slow fading colour in the dark (usually more than 5 min), and thus, once the wearer goes indoors, the lenses stay coloured for too long. A fast switching system able to achieve intense grey colourations is thus actively sought by the lens industry.

We have recently discovered that 1-vinylidene-naphthofurans exhibit curious and interesting photochromic properties. These uncoloured compounds, which can be easily synthetized, are activated by UV or sunlight, affording violet coloured species that return spontaneously to the uncoloured state, in the dark, in few minutes [17]. However, while most photochromic molecules show these properties in common organic solvents, 1-vinylidene-naphthofurans require an acidic medium, such as acidified methanolic solutions, to generate the coloured species. Furthermore, they also show photochromic properties when adsorbed in silica gel. The mechanism of the reaction behind this phenomena has been establish by NMR analysis of acidified CD_3OD solutions [18]. Thus, in methanolic solution, the UV light promotes the addition of methanol to the allene group affording an uncoloured intermediate that in the presence of acid is converted into a cationic violet dye, which returns thermally to the initial closed naphthofuran in the dark (Scheme 1). These molecules show some aspects that make them potentially interesting for application in photochromic lenses. In particular, the fast activation under sunlight providing intense colourations that fade in few minutes, in the dark, at room temperature, and the preference for a silica environment which is an advantage since most coatings are based on a siloxane network.

Although hundreds of thermally reversible photochromic compounds have been studied, only a few of them are able to generate a grey colouration, which is characterized by a constant absorption throughout the visible spectra [19,20]. Therefore to generate a grey colour the industry used mainly mixtures of photochromic compounds able to generate complementary colours, but these must exhibit similar colouration and fading kinetics, otherwise during the colouration and fading a different shade is obtained which limits the range of compatible compounds. The use of a single photochromic compound allows to overcome this matching problem. Interestingly, the visible spectra of the coloured species of 1-vinylidene-naphthofurans shows two absorption bands around 440 and 570 nm which, theoretically, can be shifted bathochromically, by introducing a conjugated substituent, to generate coloured species with a broad absorption in the UV region. In the present study, we describe the synthesis of a series of substituted 1-vinylidene-naphthofurans, with an extended conjugation and evaluate their photochromic properties, under UV light at room temperature, when dispersed in silica gel and in acidified THF solutions.



Scheme 1. Photochromic equilibrium for 1-vinylidenenaphthofuran **1** in methanolic acidified solution.

2. Results and discussion

2.1. Synthesis and characterization

1-Vinylidene-naphtho[2,1-*b*]furans can be easily prepared by reaction of substituted naphth-1-ols with 1,1,4,4-tetraphenylbut-2-yn-1,4-diol in $CHCl_3$, in the presence of a catalytic amount of *p*-toluenesulfonic acid, at room temperature, in medium yields. To prepare a set of styryl substituted naphthofurans we started with compound **2**, presenting a hydroxymethyl group at carbon 7, which can be prepared in two steps from the commercially available ethyl 6-hydroxy-2-naphthoate [18]. This compound was then oxidized with PCC affording the aldehyde **3** in good yield (69%). The Wittig reaction of this aldehyde with the ylides derived from the phosphonium salts **4a-f** afforded the 7-styryl-1-vinylidene-naphthofurans **5a-f,** as a mixture of *E-Z* isomers, in medium yield (34–89%), without any perturbation of the dihydrofuran cycle (Scheme 2).

Besides the extended aromatic signals in the ^1H NMR spectrum, these compounds show two distinctive signals in the ^{13}C NMR spectrum: a low field signal around 202 ppm, characteristic of the allene function, and a signal at 95 ppm assigned to the dihydrofuran sp^3 carbon atom.

2.2. Photochromic properties in silica gel

The 1-vinylidene-naphtho[2,1-*b*]furans **1, 2, 5a-f** do not exhibit photochromic properties when exposed to the sunlight or irradiated with UV light (254 or 365 nm), in solution or in the solid state. Nevertheless, they exhibit important photochromic properties when adsorbed in acidic silica gel, a white powder with a strong absorption below 300 nm. The dispersion of the compounds **1, 2** and **5b** in the silica gel affords a white solid, while with compounds **5a, 5c-f** a slightly yellowish powder was obtained. The UV–Vis absorption spectra of the doped silica gel samples, before and after UV irradiation, was determined using a UV–Vis spectrometer equipped with an external diffuse reflectance accessory. Compounds **1** and **2** were included in this study for comparison purposes [17,18].

A sample of silica doped with naphthofuran **2,** substituted by a hydroxymethyl group, is white with a very strong absorption in the UV region below 390 nm. After UV irradiation for 1 min using a 6 W UV lamp (365 nm), this sample develops a violet colouration, characterized by two absorption maxima in the visible region at 442 and 565 nm, the latter being stronger (Fig. 1, Table 1). The unsubstituted naphthofuran **1** exhibits a similar behavior, while the compound **3,** with a carbaldehyde group, is yellow in $CHCl_3$ solution and doesn't show photochromic properties, at room temperature, when dispersed in silica.

The silica gel doped with naphthofurans **5a-f** present a very strong absorption in the UV region which extends to near 410 nm