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Studies on photochromic benzimidazol[1,2*a*]pyrrolidin-2-ones from the condensation of 2-methyl-3-benzothienylethylidene-(isopropylidene)succinic anhydride with 1,2-diaminobenzenes

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Abstract

Novel photochromic benzimidazol[1,2*a*]pyrrolidin-2-ones, which give thermally stable highly coloured photochromes, have been synthesised by condensation of 2-methyl-3-benzothienylethylidene(isopropylidene)succinic anhydride with 1,2-diaminobenzene and its 4,5-dimethyl and 4,5-dimethoxy derivatives. The photochromic properties are reported.

Keywords: Photochromism; Fulgide; 1,2-Diaminobenzene; Benzimidazol[1,2*a*]pyrrolidin-2-one

1. Introduction

Certain derivatives of fulgides [1] and diarylethylenes [2] are known to give highly coloured thermally stable photochromes on exposure to ultraviolet light. The photochromes undergo the reverse reactions when irradiated with visible light. These photochromic compounds have attracted much attention due to their potential industrial applications, including re-writeable optical memory media [3]. For these applications, the photochromic compounds should possess fatigue resistance, particularly to hydrolysis of the anhydride group in these systems.

A useful starting point for improving fatigue resistance and enhancing the photochromic properties is to replace either of the oxygen atoms of the anhydride moiety with other functional groups.

For example, Heller et al. [4] reported that replacement of one of the carbonyl groups in fulgides by a dicyanomethylene group (=C(CN)$_2$) gave a new class of thermally stable photochromic compounds which were near infrared active. Fulgides react with primary aliphatic and aromatic amines to give either fulgimides [5] or isofulgimides [6]. Fulgimides display excellent photochromic properties as well as much greater resistance to hydrolysis than their corresponding fulgides [7].

In 1972, Young [8] reported that phthalic anhydride condensed with 1,2-diaminobenzene (**1**, R = H) to give *N*-4-(*o*-aminophenyl)phthalamic acid (**2**), which eliminates water to form *N*-(*o*-aminophenylphthalimide (**3**) and 2-(*o*-carboxyphenyl)benzimidazole (**4**). At 200 °C, compounds (**3**) and (**4**) dehydrate to yield 11-*H*-isoindolo[2,1-*a*]benzimidazol-11-one (**5**) (Scheme 1).

In this paper, we report the syntheses of new photochromic benzimidazol[1,2*a*]pyrrolidin-2-one derivatives, obtained by condensation of *Z*-fulgides, *Z*-(2-methyl-3-benzothienylethylidene(isopropylidene)succinic anhydrides) (**14**) with 1,2-diaminobenzene (**1**, R = H), 4,5-dimethyl-1,2-diaminobenzene (**1**, R = Me) and 4,5-dimethoxy-1,2-diaminobenzene (**1**, R = MeO).

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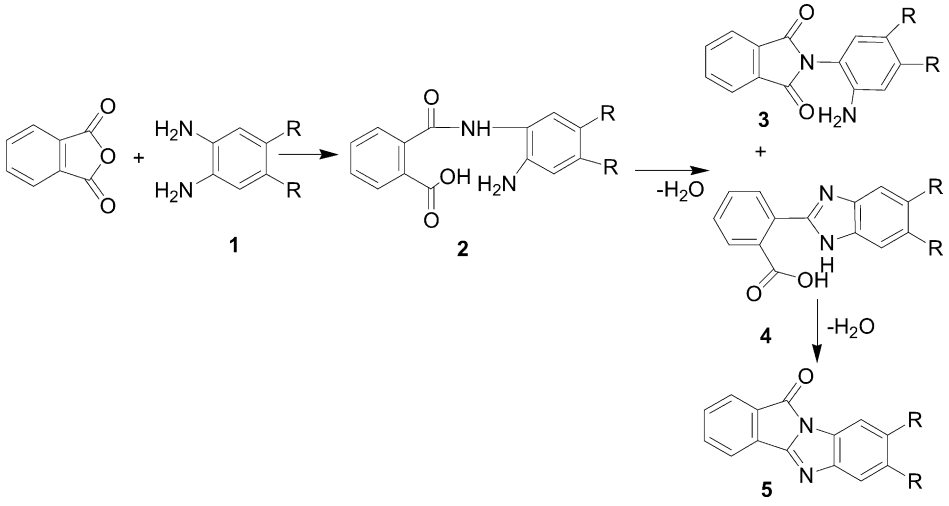

Scheme 1. The reaction of phthalic anhydride with 1,2-diaminobenzene (**1**, R = H).

2. Results and discussions

A mixture of *Z*- and *E*-fulgides (**14** and **15**) were prepared by the Stobbe condensation of 2-methyl-3-acetylbenzothiophene (**8**) with diethyl isopropylidene succinate (**11**), followed by hydrolysis and cyclisation with acetyl chloride (Scheme 2). On irradiation (365 nm), *Z*-fulgide (**14**) in toluene isomerised to *E*-fulgide (**15**), which photocyclised to the thermally stable red photochrome, 4,4*a*-dihydro-1,4,4,4*a*-tetramethyldibenzo[*b*,*d*]thiophene-2, 3-dicarboxylic anhydride (**16**). Photochrome (**16**) underwent the reverse reaction to fulgide (**15**) on exposure to white light (Scheme 4). The absorption spectra of (**14**) and its photostationary states of 365-nm light irradiation are shown in Fig. 1.

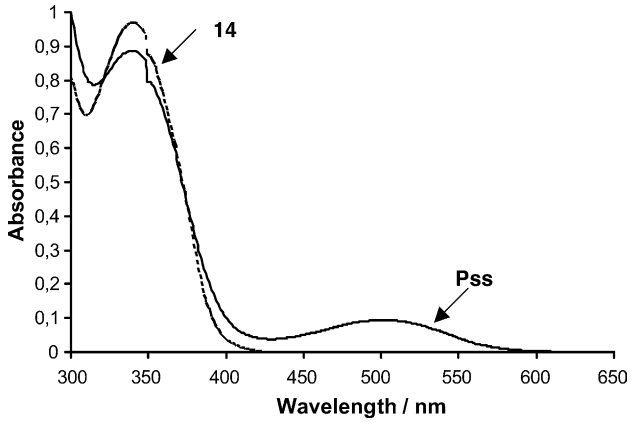

Fig. 1. Absorption spectral change of (**14**) in toluene (1×10^{-4} mol dm^{-3}) irradiated with 365 nm light.

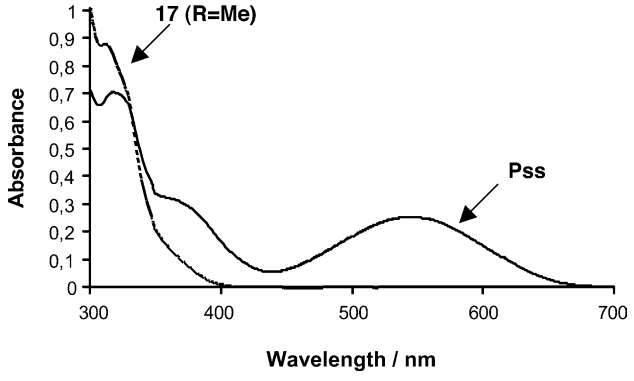

Fig. 2. Absorption spectral change of (**17**) (R = Me) in toluene (1×10^{-4} mol dm^{-3}) irradiated with 365 nm light.

Photochrome (**16**) in toluene showed a hypsochromic shift of its long wavelength absorption band (λ_{max} 500 nm) compared to the photochrome, 7,7*a*-dihydro-2,4,7,7, 7*a*-pentamethylbenzothiophene-5,6-dicarboxylic anhydride (λ_{max} 520 nm) in toluene [9], presumably due to affect of benzannelation on the dipolar character of the coloured form.

Because the non-symmetric *Z*-fulgide (**14**) was reacted with symmetrical diaminobenzene (**1**), two products were expected, depending on which carbonyl group of the anhydride ring was involved in the reaction (Scheme 3). If condensation occurred at the α carbonyl, an α-isomer would be formed and if the β carbonyl was involved, a β-isomer was formed. When *Z*-fulgide (**14**) and 1,2-diaminobenzene (**1**, R = H, Me or MeO) were boiled in toluene, three new spots were observed on TLC.[i] The upper two spots were photochromic. The component of the lowest spot could not be isolated or identified.

[i] The reaction of *Z*-fulgide (**14**) with 1,2-diaminobenzene (**1**) gave three new spots on TLC (in ethyl acetate (50%) and hexane). α-*Z*-Benzimidazol[1,2*a*]pyrrolidin-2-one (**17**, R = H) Rf 0.60; β-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one (**20**, R = H) Rf 0.73 and unidentified non-photochromic component Rf 0.18; α-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one (**17**, R = Me) Rf 0.66; β-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one(**20**, R = H) Rf 0.74 and unidentified photochromic component Rf 0.5; α-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one (**17**, R = MeO) Rf 0.47; β-*Z*-benzimidazol[1,2*a*]pyrrolidin-2-one (**20**, R = MeO) Rf 0.58; and unidentified photochromic component Rf 0.3.