Chemistry of Heterocyclic Compounds, Vol. 42, No. 8, 2006

SYNTHESIS AND SPECTRAL KINETIC INVESTIGATION OF SOLUTIONS OF PHOTOCHROMIC THIENYLFULGIMIDES

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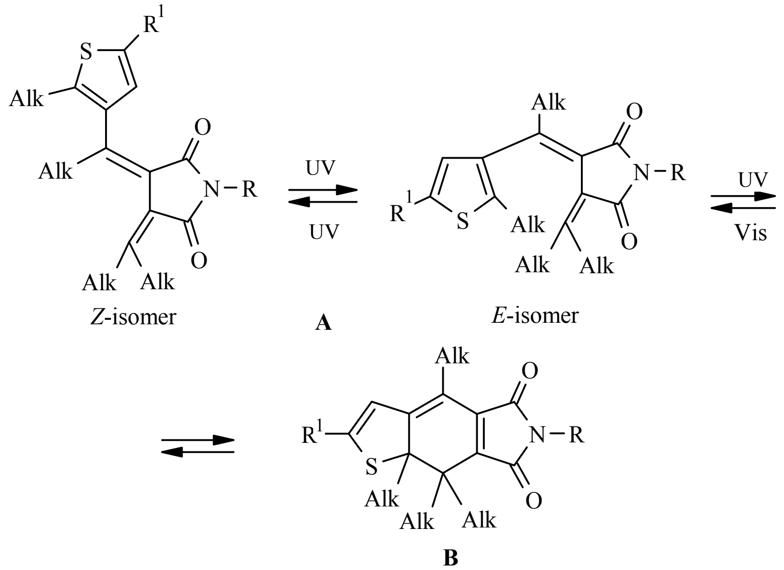
A convenient method has been developed for the synthesis of previously unknown photochromic 1-amino-3-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)pyrrolidine-2,5-dione, from which photochromic Schiff's bases were obtained. A spectral kinetic investigation of the photochromism of the thienylfulgimides obtained has been carried out.

Keywords: 3-thienylfulgides, fulgimides, photochromism, photochromic hybrids.

Fulgimides are considered as promising light-sensitive components of photochromic recording media for operative optical memory [1-8]. Usually they test thermally irreversible but photochemically there are reversible conversions between open **A** and cyclic **B** forms. We emphasize that the initial form **A**, in its turn, exists as a mixture of interconverting *Z*- and *E*-isomers under the action of UV light, however only the latter possesses photochromic properties on the strength of its conformation.



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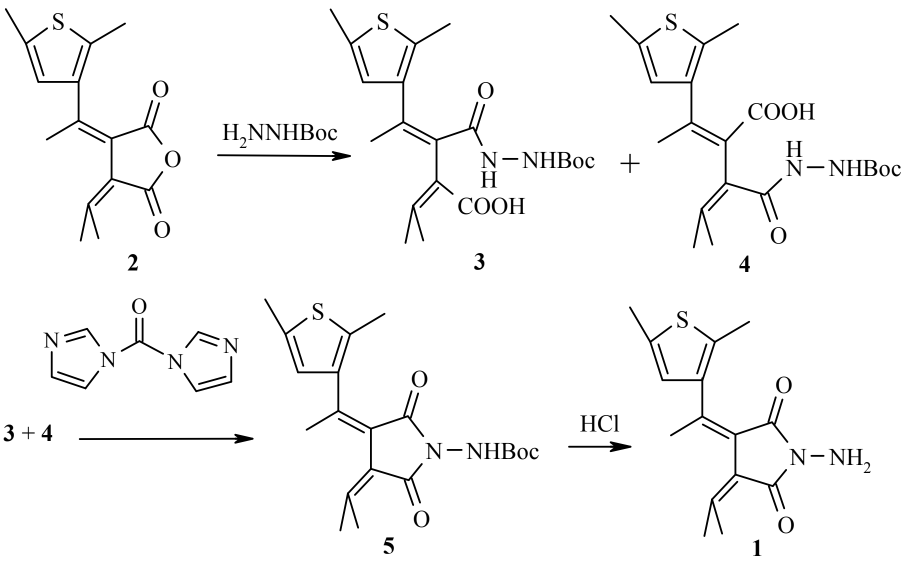
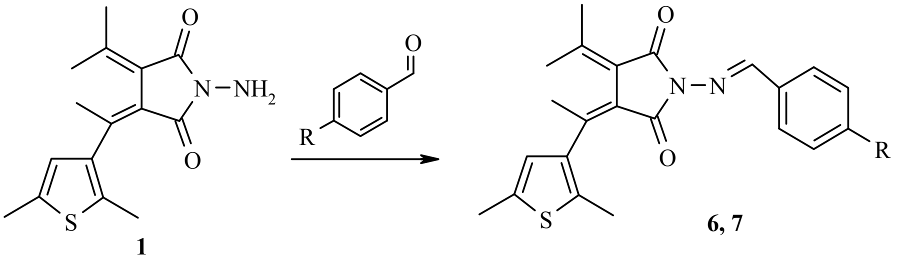
The aim of the present work is the synthesis and preliminary spectral kinetic investigation of the photochromism of a series of new 3-thienylfulgimides. Fulgimide **1** seemed to us an extremely promising compound. It is assumed that this substance will possess photochromic properties and in addition will readily form Schiff's bases, also potentially photochromic [9]. It was possible to design the synthesis of previously unknown fulgimide derivatives containing aldimine fragments.

However we were unsuccessful in obtaining aminofulgimide **1** by the reaction of fulgide **2** [10] with free hydrazine or hydrazine hydrate in one step as a result of the formation of difficultly separable multicomponent mixtures, so a three-step synthesis was put into effect.



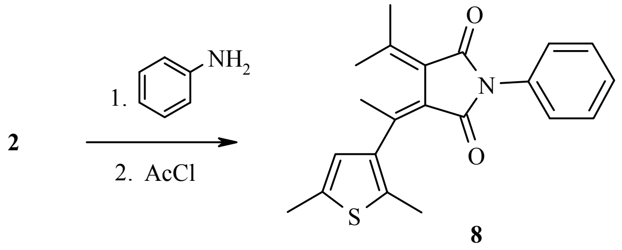
The interaction of the initial fulgide **2** with N-Boc-hydrazine on boiling in benzene leads to a mixture of the isomeric *E*- and *Z*-hydrazido acids **3** and **4** in 84% overall yield. However cyclization of the obtained amino acids, by methods described in the literature based on the use of acid chlorides or acid anhydrides to obtain fulgimides [11], proved to be impossible in view of the fact that removal of the Boc protection occurs in acidic medium with subsequent complex transformation of the hydrazide function. This obliged us to search for other cyclizing reagents.

We proposed N,N'-carbonyldiimidazole as such an effective agent, which permitted the formation of N-Boc-aminofulgimide **5** in 82% yield under mild conditions [12]. Subsequent fission of the Boc group by the action of alcoholic HCl solution leads practically quantitatively to N-aminofulgimide **1**. Interaction of the latter with *p*-chloro- and *p*-nitrobenzaldehydes in anhydrous ethanol in the presence of a catalytic amount of *p*-toluenesulfonic acid gives products **6** and **7** in yields of 53 and 86% respectively.



6 R = Cl, **7** R = NO_2

Fulgimide **8** was obtained as a standard compound for comparative analysis of the spectral kinetic characteristics of the compounds obtained by us.



The reaction was carried out by the known method of [13] by condensing fulgide **1** with aniline with the formation of the corresponding amino acid and cyclization of the latter with acetyl chloride, which made it possible to obtain fulgimide **8** in 43% yield.

The spectral kinetic characteristics of the investigated fulgimides are given in Table 1. In the absorption spectra of the open form **A** of compounds **1, 5-8** in toluene bands were observed with a maximum in the 290-330 nm region. The cyclic form of all the compounds absorbs in the visible region of the spectrum with band maxima in the range 520-540 nm (see Table 1).

Investigation of the kinetics of the thermal relaxation of the photoinduced cyclic form **B** into the initial open form **A** for all the compounds showed that both forms are thermally stable for at least one month under conditions of storing solutions of them in well sealed vessels in the dark.

TABLE 1. Spectral Kinetic Data of the Photochromic Conversions of Fulgimides in Toluene*

Compound	λ^{A}_{max}, nm	λ^{B}_{max}, nm	D^{phot}_{max}	$\varphi^{phocol}/\varphi_8$	$\varphi^{phodec}/\varphi_8$	$t_{0,5}^{phodeg}$, sec
8	330 dec	522	0.75	1.00	1.00	70
1	325	520	0.90	0.68	1.80	70
5	330	530	0.70	0.53	3.20	80
6	290	540	0.61	0.14	4.10	95
7	305	540	0.65	0.27	5.00	100

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* λ^{A}_{max} and λ^{B}_{max} are the maxima of the absorption bands of the open **A** and cyclic **B** forms; D^{phot}_{max} is the maximum photoinduced optical density at the maximum of the absorption band of the cyclic form **B**; $t_{0.5}^{phodeg}$ is the time for the change in the size of the photoinduced optical density at the maximum of the absorption band of the cyclic form to half in the process of irreversible photochemical conversion (photodegradation) of the substance; $\varphi^{phocol}/\varphi_8$ and $\varphi^{phodec}/\varphi_8$ are the quantum yields for the processes of photocoloration and photodecoloration relative to the quantum yield of the same processes for compound **8** respectively.

EXPERIMENTAL

The ^1H NMR spectra were recorded on a Bruker WM 250 (250 MHz) radiospectrometer in DMSO-d_6 (compounds **3** and **4**) and in $CDCl_3$ (compounds **1, 5-7**), internal standard was TMS. The mass spectra (EI) were taken on a Kratos MS 30 instrument with direct insertion of samples into the ion source, ionizing voltage was 70 eV, emission current 0.1 mA, temperature of the ionization chamber was 250°C. Melting points were measured on a Boetius microscope stage and are not corrected. Analysis of reaction mixtures and a check on the purity of the isolated products was carried out by TLC on Silufol UV 254 plates, eluent was ethyl acetate–hexane.

Investigation of the photochromic properties of compounds **1, 5-8** was carried out in toluene solution. The concentration of compounds in solution was $c = 2 \times 10^{-4}$ M. Measurements were carried out in cuvettes of thickness 3 mm. The absorption spectra of the open and cyclic forms were measured on a Shimadzu UV-Vis or Carey (Varian) spectrophotometers in the spectrum range 200-800 nm. The cyclic form was obtained after photoactivation of a solution by irradiation with a DRSh-250 mercury lamp through a UV light filter separating radiation with $\lambda = 313$ nm. Photodecoloration of a solution was achieved on irradiation with filtered radiation of $\lambda = 546$ nm. The kinetics of photocoloration of fulgimide solutions were measured at the wavelength of the absorption band maximum on irradiation of solutions of these compounds first decolorized by the same radiation. The kinetics of photodecoloration were measured on irradiation of a first colored solutions of these compounds with radiation with lead lines of a DPSh 250 lamp, separated with the aid of the appropriate glass filters. Starting from the obtained photoconversion constants, allowing for the quanta of light absorbed by the solutions, quantum yields were determined for photocoloration and photodecoloration of all the synthesized compounds relative to the corresponding quantum yields of compound **8**.

3-{[(*tert*-Butoxycarbonyl)hydrazino]carbonyl}-2(*Z*)-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-methyl-3-pentenoic Acid (3) and 3(*Z*)-{[(*tert*-Butoxycarbonyl)hydrazino]carbonyl}-2-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-methyl-3-pentenoic Acid (4). A solution of compound **1** (2 g, 7.2 mmol) and N-(*t*-butoxycarbonyl)hydrazine (1 g, 7.5 mmol) in benzene (30 ml) was refluxed for 10 h. The benzene was removed on the rotary evaporator, the residue was subjected to chromatography on SiO_2, using as eluent a mixture of hexane with ethyl acetate 2:1, and then pure ethyl acetate. A mixture of compounds **3** and **4** (2.5 g, 84%) was obtained in a ratio of 1:1.

Compound 3. ^1H NMR spectrum, δ, ppm: 1.39 [9H, s, $C(CH_3)_3$]; 1.74 (3H, s, CH_3); 1.84 (3H, s, CH_3); 2.11 (3H, s, CH_3); 2.19 (3H, s, CH_3); 2.35 (3H, s, CH_3); 6.52 (1H, s, H thioph.); 8.65 (1H, s, NH); 9.35 (1H, s, NH).

Compound 4. ^1H NMR spectrum, δ, ppm: 1.31 [9H, s, $C(CH_3)_3$]; 1.72 (3H, s, CH_3); 1.83 (3H, s, CH_3); 2.01 (3H, s, CH_3); 2.18 (3H, s, CH_3); 2.35 (3H, s, CH_3); 6.51 (1H, s, H thioph.); 8.65 (1H, s, NH); 9.35 (1H, s, NH).

Mass spectrum (mixture of compounds **3** and **4**), *m/z*: 408 $[M]^+$, 319, 277, 91, 57. Found, %: C 58.62; H 6.55; N 6.74. $C_{20}H_{28}N_2O_5S$. Calculated, %: C 58.80; H 6.91; N 6.86.

1-(*tert*-Butoxycarbonylamino)-3(*Z*)-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)-pyrrolidine-2,5-dione (5). The obtained mixture of hydrazido acids **3** and **4** was dissolved in THF (50 ml) and N,N'-carbonyldiimidazole (1.03 g, 6.3 mmol) was added. The reaction mixture was stirred for 2 h at room temperature, and left overnight. The THF was distilled off. After chromatography on SiO_2 (hexane–ethyl acetate, 5:1) compound **5** (1.875 g, 82%) was obtained as light yellow crystals; mp 178-180°C. ^1H NMR spectrum, δ, ppm: 1.45 [9H, s, $C(CH_3)_3$]; 1.98 (3H, s, CH_3); 2.08 (3H, s, CH_3); 2.3 (3H, s, CH_3); 2.41 (3H, s, CH_3); 2.44 (3H, s, CH_3); 6.31 (1H, s, NH); 6.51 (1H, s, H thioph.). Mass spectrum, *m/z*: 391 $[M+1]^+$, 390 $[M]^+$, 319, 275, 260, 217, 203, 189, 137, 112, 57. Found, %: C 61.44; H 6.94; N 7.25; S 8.04. $C_{20}H_{26}N_2O_4S$. Calculated, %: C 61.52; H 6.71; N 7.17; S 8.21.

1-Amino-3(*Z*)-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)pyrrolidine-2,5-dione (1). A solution of compound **5** (0.5 g, 1.3 mmol) in methanol (75 ml) saturated with HCl was kept at room temperature for 12 h. The reaction mixture was evaporated to dryness on the rotary evaporator, the residue dissolved in methanol (30 ml), and 5 N NH_3 in methanol (10 ml) was added. The mixture was evaporated to dryness on the rotary evaporator. THF (30 ml) was added to the residue, which was filtered, and the solid was washed on the filter with THF (2 × 20 ml). The filtrate was evaporated on the rotary evaporator and compound **5** (0.36 g, 97%) was obtained as light yellow crystals; mp 172-173°C. ^{1}H NMR spectrum, δ, ppm: 1.96 (3H, s, CH_3); 2.06 (3H, s, CH_3); 2.29 (3H, s, CH_3); 2.39 (3H, s, CH_3); 2.42 (3H, s, CH_3); 4.18 (2H, s, NH_2); 6.50 (1H, s, H thioph.). Mass spectrum, *m/z*: 291 $[M+1]^+$, 290 $[M]^+$, 275, 217, 203, 189. Found, %: C 62.25; H 6.44; N 9.55. $C_{15}H_{18}N_2O_2S$. Calculated, %: C 62.04; H 6.25; N 9.65.

1-[1-(4-Chlorophenyl)methylen]amino-3(*Z*)-[1-(2,5-dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)pyrrolidine-2,5-dione (6). *p*-Chlorobenzaldehyde (0.05 g, 0.35 mmol), *p*-toluenesulfonic acid (0.01 g), and molecular sieve 3Å (0.5 g) were added to a solution of compound **1** (0.1 g, 0.34 mmol) in anhydrous ethanol (5 ml). The reaction mixture was refluxed for 8 h, filtered, and the solid washed on the filter with chloroform. The filtrate was evaporated to dryness on the rotary evaporator, and the residue subjected to chromatography on SiO_2 (hexane–ethyl acetate, 6.5:1). Compound **6** (0.075 g, 53%) was obtained; mp 164-167°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.01 (3H, s, CH_3); 2.11 (3H, s, CH_3); 2.35 (3H, s, CH_3); 2.42 (3H, s, CH_3); 2.48 (3H, s, CH_3); 6.55 (1H, s, H thioph.); 7.37 (2H, d, J = 8.2, H arom.); 7.76 (2H, d, J = 8.2, H arom.); 9.27 (1H, s, NH). Mass spectrum, *m/z*: 413 $[M+1]^+$, 412 $[M]^+$, 397, 258, 189, 137, 59. Found, %: C 63.95; H 5.34; N 6.65. $C_{22}H_{21}ClN_2O_2S$. Calculated, %: C 63.99; H 5.13; N 6.78.

3(*Z*)-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)-1-[1-(4-nitrophenyl)methylen]-aminopyrrolidine-2,5-dione (7). *p*-Nitrobenzaldehyde (0.05 g, 0.35 mmol), *p*-toluenesulfonic acid (0.01 g), and molecular sieve (4Å) (0.5 g) were added to a solution of compound **1** (0.1 g, 0.34 mmol) in anhydrous ethanol (5 ml). The reaction mixture was refluxed for 8 h, filtered, and the solid was washed on the filter with chloroform. The filtrate was evaporated to dryness on the rotary evaporator, and the residue subjected to chromatography on SiO_2 (hexane–ethyl acetate, 6.5:1). Compound **7** (0.125 g, 86%) was obtained; mp 145-146°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.03 (3H, s, CH_3); 2.13 (3H, s, CH_3); 2.33 (3H, s, CH_3); 2.42 (3H, s, CH_3); 2.51 (3H, s, CH_3); 6.56 (1H, s, H thioph.); 7.97 (2H, d, J = 8.3, H arom.); 8.25 (2H, d, J = 8.3, H arom.); 9.52 (1H, s, NH). Mass spectrum, *m/z*: 424 $[M+1]^+$, 423 $[M]^+$, 408, 258, 189, 59. Found, %: C 62.55; H 5.14; N 9.66. $C_{22}H_{21}N_3O_4S$. Calculated, %: C 62.40; H 5.00; N 9.92.

3(*Z*)-[1-(2,5-Dimethyl-3-thienyl)ethylidene]-4-(1-methylethylidene)-1-phenylpyrrolidine-2,5-dione (8). Anhydride **1** (1.1 g, 4.4 mmol) was added to a solution of freshly distilled aniline (0.4 g, 4.4 mmol) in dry benzene (30 ml), and the reaction mixture refluxed for 6 h. At the end of boiling the precipitated crystals were filtered off, dissolved in dry methylene chloride (30 ml), and acetyl chloride (20 ml, 280 mmol) was added. The reaction mixture was stirred for 2 h at room temperature. The solvent and excess of acetyl chloride were distilled off on the rotary evaporator. The light brown amorphous powder was subjected to chromatography on SiO_2 (hexane–ethyl acetate, 4:1), and light yellow crystals of compound **8** (0.61 g, 43%) were obtained; mp 130-133°C (chloroform–petroleum ether) (lit. mp 131-133°C [13]). Mass spectrum, *m/z* 351 $[M]^+$.

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