

SHORT
COMMUNICATIONSSynthesis and Photochromic Properties of Fulgides Based
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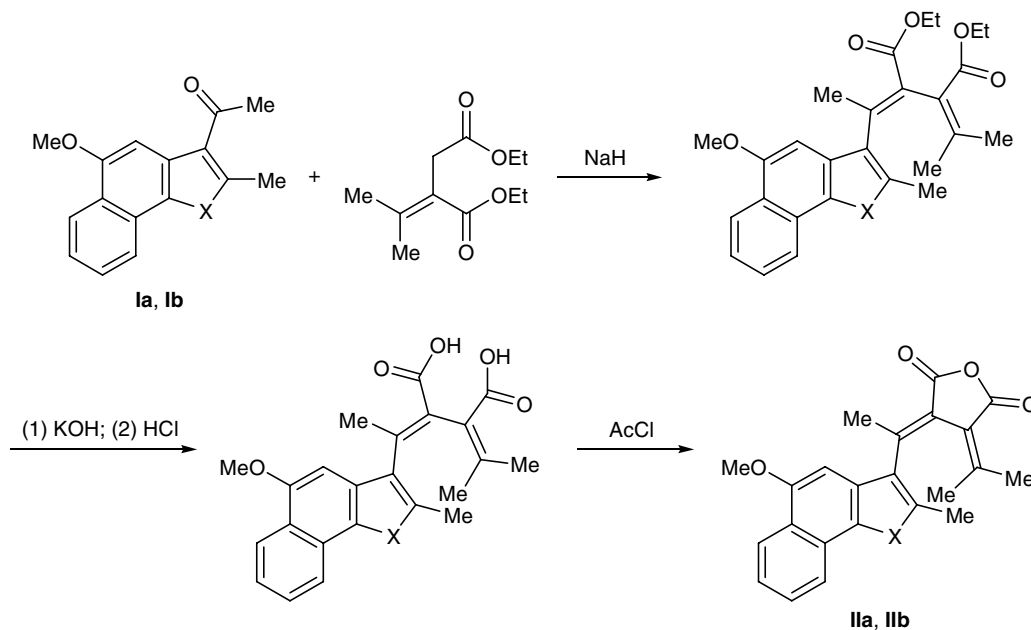
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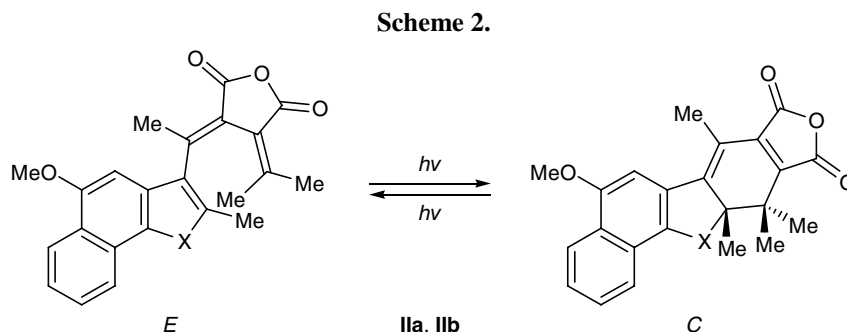
Heteroaromatic fulgides and fulgimides are among the most promising photochromic compounds for three-dimensional optical data storage devices and optical molecular switches due to high stability of their initial and photoinduced forms [1, 2]. However, there are no data on fulgides based on naphtho-fused five-membered heterocyclic compounds. With the goal of studying compounds of this sort, we have synthesized fulgides **IIa** and **IIb** by the Stobbe condensation of 1-(5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl)-ethanone (**Ia**) and 1-(5-methoxy-2-methyl-1-phenyl-

1*H*-benzo[*g*]indol-3-yl)ethanone (**Ib**) with diethyl 2-isopropylidenebutanedioate in the presence of sodium hydride [3] (Scheme 1).

On the basis of the IR and ¹H NMR spectra, the isolated products were assigned the structure of 3-isopropylidene-4-{1-(5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl)ethylidene}tetrahydrofuran-2,5-dione (**IIa**) and 3-isopropylidene-4-{1-(5-methoxy-2-methyl-1-phenyl-1*H*-benzo[*g*]indol-3-yl)ethylidene}tetrahydrofuran-2,5-dione (**IIb**). Both compounds are *E* isomers with respect to the C⁴=C heterylethylidene double

Scheme 1.





bond, as follows from the presence in their ^1H NMR spectra of a singlet from the $\text{C}^4=\text{CCH}_3$ protons at δ 2.79 ppm (**IIa**) and 2.88 ppm (**IIb**) [4].

The electronic absorption spectrum of fulgide **IIa** (*E*) in toluene contains a long-wave band with its maximum at λ 344 nm ($\epsilon = 10100 \text{ l mol}^{-1} \text{ cm}^{-1}$). Fulgide **IIb** (*E*) in toluene absorbs at longer wavelengths: its absorption maximum is located at λ 373 nm ($\epsilon = 10800 \text{ l mol}^{-1} \text{ cm}^{-1}$). The *E* isomers of fulgides **IIa** and **IIb** are capable of undergoing photoinduced electrocyclic reaction shown in Scheme 2. Irradiation of solutions of fulgides **IIa** and **IIb** with UV light (λ 365 nm) corresponding to the long-wave absorption region of their *E* isomers results in coloration typical of cyclic forms *C* [5, 6]. The colored form (*C*) of fulgide **IIa** absorbs at λ_{max} 552 nm. The photoinduced form of compound **IIb** absorbs at a considerably longer wavelength: its absorption maximum is located at λ 643 nm. Cyclic isomers *C* of fulgides **IIa** and **IIb** are characterized by high thermal stability in toluene: the reverse thermal reaction $\text{C} \rightarrow \text{E}$ did not occur at 293 K over a period of 72 h. Irradiation of solutions of colored *C*-forms of **IIa** and **IIb** in the visible region (λ 546, 578 nm) leads to decoloration, and the initial absorption spectra (before UV irradiation) are restored, obviously as a result of photoinduced ring opening $\text{C} \rightarrow \text{E}$. The colored cyclic isomers of **IIa** and **IIb** were found to exhibit fluorescence. The fluorescence maxima in toluene are located at λ 648 nm for fulgide **IIa** and at λ 791 nm for **IIb**. The fluorescence excitation spectra of isomers *C* showed that their $\text{S}_0 \rightarrow \text{S}_2$ transition bands are overlapped by the $\text{S}_0 \rightarrow \text{S}_1$ transition bands of the *E* isomers; therefore, complete conversion of the latter into the colored cyclic form cannot be attained. UV irradiation leads to a photostationary equilibrium state.

3-Isopropylidene-4-{1-(5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl)ethylidene}tetrahydrofuran-2,5-dione (IIa**).** A solution of 2 g (8 mmol) of 1-(5-methoxy-2-methylnaphtho[1,2-*b*]furan-3-yl)ethanone (**Ia**), 1.9 g (9 mmol) of diethyl 2-isopropylidenebutanedioate, and 1 ml of diisopropylamine in

20 ml of tetrahydrofuran was added under stirring at room temperature to a suspension of 0.8 g (30 mmol) of sodium hydride in 10 ml of tetrahydrofuran. The mixture was stirred for 2 h at 50°C, the solvent was distilled off under reduced pressure (water-jet pump), the residue was treated with 10% hydrochloric acid, and the precipitate was filtered off. It was transferred into another flask, a 10% solution of potassium hydroxide in methanol was added, and the mixture was heated for 2 h under reflux, diluted with water, and filtered. The filtrate was acidified with 10% hydrochloric acid, and the precipitate was filtered off, dried in air, and dissolved in 1 ml of acetyl chloride on heating. Excess acetyl chloride was distilled off under reduced pressure, and the residue was purified by column chromatography on Silufor using chloroform as eluent; the product was additionally recrystallized from toluene. Yield 0.24 g (8%), yellow crystals, mp 199–200°C. UV spectrum, λ_{max} , nm: 345, 360–380. IR spectrum, ν , cm^{-1} : 1790, 1730. ^1H NMR spectrum, δ , ppm: 1.12 s, 2.20 s, 2.21 s, and 2.80 s (3H each, CH_3); 3.98 s (3H, OCH_3); 6.7 s (1H, CH); 7.5–8.3 (4H, H_{arom}). Found, %: C 76.02; H 5.13. $\text{C}_{22}\text{H}_{18}\text{O}_4$. Calculated, %: C 76.29; H 5.24.

3-Isopropylidene-4{1-(5-methoxy-2-methyl-1-phenyl-1*H*-benzo[*g*]indol-3-yl)ethylidene}tetrahydrofuran-2,5-dione (IIb**).** A solution of 4 g (12 mmol) of 1-(5-methoxy-2-methyl-1-phenyl-1*H*-benzo[*g*]indol-3-yl)ethanone (**Ib**), 2.8 g (13 mmol) of diethyl 2-isopropylidenebutanedioate, and 1.5 ml of diisopropylamine in 20 ml of tetrahydrofuran was added under stirring at room temperature to a suspension of 1.2 g (45 mmol) of sodium hydride in 10 ml of tetrahydrofuran. The mixture was stirred for 2 h at 50°C, the solvent was distilled off under reduced pressure (water-jet pump), the residue was treated with 10% hydrochloric acid, and the precipitate was filtered off. It was transferred into another flask, a 10% solution of potassium hydroxide in methanol was added, and the mixture was heated for 2 h under reflux, diluted with

water, and filtered. The filtrate was acidified with 10% hydrochloric acid, and the precipitate was filtered off, dried in air, and dissolved in 1.2 ml of acetyl chloride on heating. The solvent was distilled off under reduced pressure, and the residue was purified by column chromatography on Silufor using chloroform as eluent; the product was additionally recrystallized from toluene. Yield 0.88 g (16%), yellow–green crystals, mp 182–184°C. UV spectrum, λ_{max} , nm: 345, 370–380. IR spectrum, ν , cm^{-1} : 1800, 1750. ^1H NMR spectrum, δ , ppm: 1.12 s, 2.20 s, 2.21 s, and 2.80 s (3H each, CH_3); 3.98 s (3H, OCH_3); 6.7 s (1H, CH); 7.5–8.3 m (4H, H_{arom}). Found, %: C 76.61; H 6.12; N 3.19. $\text{C}_{29}\text{H}_{27}\text{NO}_4$. Calculated, %: C 76.80; H 6.00; N 3.09.

The electronic absorption spectra were measured on a Varian Carry-100 spectrophotometer. The photolysis was performed using a DRSh-250 high-pressure mercury lamp equipped with a set of interference filters to isolate required wavelengths; cell path length 10 mm; concentration (toluene) 2×10^{-5} M. The IR spectra were recorded on a Specord 75IR spectrometer from samples dispersed in mineral oil. The ^1H NMR spectra were obtained on a Varian Unity-300 instrument (300 MHz) from solutions in $\text{DMSO}-d_6$.

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REFERENCES

1. Bren', V.A., Dubonosov, A.D., and Minkin, V.I., *Vestn. Yuzhn. Nauch. Tsentra Ross. Akad. Nauk*, 2005, no. 2, p. 58.
2. Yokoyama, Y., *Chem. Rev.*, 2000, vol. 100, p. 1717.
3. Stobbe, H., *Chem. Ber.*, 1905, vol. 38, p. 3672.
4. Heller, H.G. and Oliver, S.N., *J. Chem. Soc., Perkin Trans. I*, 1981, no. 2, p. 197.
5. Minkin, V.I., Medyantseva, E.A., Lyashik, O.T., Metelitsa, A.V., Andreeva, I.M., Knyazhanskii, M.I., and Volbushko, N.V., *Khim. Geterotsikl. Soedin.*, 1986, p. 1569.
6. Metelitsa, A.V., Lyashik, O.T., Aldoshin, S.M., Kozi-na, O.A., Volbushko, N.V., Medyantseva, E.A., Knyazhanskii, M.I., Minkin, V.I., and Atovmyan, A.O., *Khim. Geterotsikl. Soedin.*, 1990, p. 33.