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V.A. Tartakovskii on the 70th Anniversary of His Birth

Photochromic Dihetarylethenes: XVII.* New Synthesis of Photochromic *N*-Alkyldithienylmaleimides**

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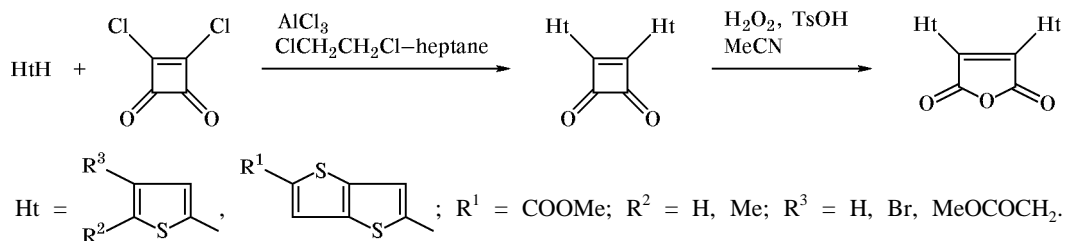
Abstract—A new convenient procedure for the synthesis of photochromic *N*-alkyldithienylmaleimides was developed on the basis of the reaction of 3,4-bis(2,5-dimethyl-3-thienyl)furan-2,5-dione with primary amines. Photochromic properties of the products were examined.

Rapid development of computer technology in the last decade has stimulated vast studies in the field of thermally irreversible photochromes on the basis of dihetarylethenes [2–5]. Among the latter, important compounds are dihetaryl-substituted derivatives of maleic anhydride and maleimide [5, 6]. Up to now, their synthesis was quite laborious and low efficient (the overall yields of the products were poor), which restricted search for new photochromic systems suitable for creation of three-dimensional optical memory materials and optically controlled molecular switches. The known methods for preparation of dihetarylfurandiones (maleic anhydride derivatives) and dihetarylpyrrolediones (maleimide derivatives) are

based as a rule on the reaction of thienylacetyl chloride with 2-thienyl-2-oxoacetic acid or its amides; they include six steps, and the overall yield is as poor as 4–6% [5–7].

We recently proposed a new approach to the synthesis of dihetarylmaleic anhydrides, which involves the Friedel–Crafts reaction of thiophene and thieno-[3,2-*b*]thiophene derivatives with 3,4-dichlorocyclobutane-1,2-dione [8, 9] and subsequent oxidation of the condensation products according to Baeyer–Villiger [8, 10] (Scheme 1). The procedure is simple, and it ensures high overall yields of the products (more than 55%, calculated on the initial dimethylthiophene or thienothiophene derivative). This makes dithienyl

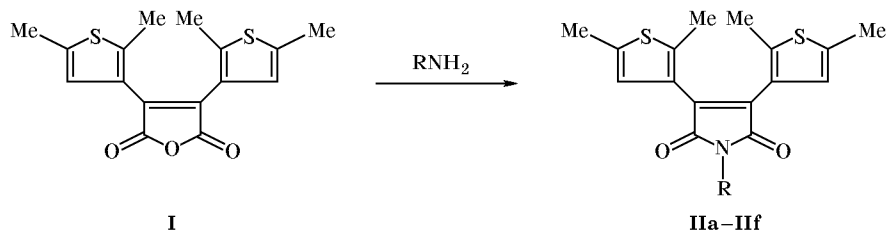
Scheme 1.



* For communication XVI, see [1].

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Scheme 2.



R = H (**a**), Me (**b**), Bu (**c**), PhCH₂ (**d**), (CH₂)₂OH (**e**), (CH₂)₆OH (**f**).

derivatives of maleic anhydride accessible compounds which attract interest as potential photochromes and are convenient starting materials for one-step transformation into the corresponding maleimides.

The goal of the present study was to develop a procedure for preparation of 1-alkyl-3,4-bis(2,5-dimethyl-3-thienyl)pyrrole-2,5-diones by reaction of 3,4-bis(2,5-dimethyl-3-thienyl)furan-2,5-dione with primary amines and to examine photochromic properties of the resulting maleimide derivatives.

We found that 3,4-bis(2,5-dimethyl-3-thienyl)furan-2,5-dione (**I**) reacts with ammonium acetate, aliphatic primary amines, and benzylamine in anhydrous methanol or ethanol in the temperature range from 20 to 80°C to afford maleimides **IIa-III** in 67–90% yield (Scheme 2). In all cases the reaction occurred in one step: no intermediate maleamic acid derivatives were detected. The structure of products **IIa-III** was confirmed by the ¹H NMR and mass spectra and elemental analyses.

Photochromic properties of dithienylpyrrolediones **IIa-III** were examined in acetonitrile solution. As expected, all compounds **IIa** turned out to be capable of undergoing reversible isomerization under UV irradiation (Scheme 3). Table contains the absorption maxima of their open (**A**) and cyclic (**B**) forms. It is seen that isomers **A**, as well as **B**, of all maleimides **IIa-III** are characterized by fairly similar absorption maxima and shapes of the absorption curves.

Preliminary experiments showed that the degree of conversion of isomer **B** of compound **IIb** into **A** in

the dark is as low as 1% in 3 days, i.e., the transformation is characterized by a considerable thermal irreversibility. Figure illustrates variation of a typical absorption spectrum (compound **IIe**) under UV irradiation ($\lambda = 365$ nm).

Thus we have developed a new convenient procedure for synthesizing photochromic dithienylethenes having a maleimide fragment as bridging group.

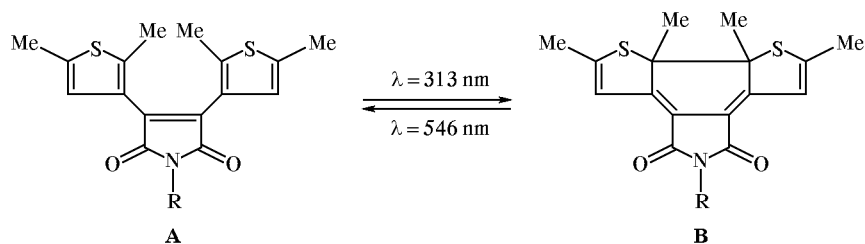
EXPERIMENTAL

The ¹H and ¹³C NMR spectra were recorded on Bruker AC-200, Bruker WM-250, and Bruker AM-300 spectrometers using CDCl₃ as solvent. The mass spectra (electron impact, 70 eV) were run on a Kratos instrument with direct sample admission into the ion source. The melting points were determined using a Boetius microscope and were not corrected.

The progress of reactions was monitored by TLC on Silicagel 60 F₂₅₄ plates (Merck) using petroleum ether (bp 40–70°C)–ethyl acetate as eluent. Commercial (from Aldrich) anhydrous methanol (99.9%), anhydrous ethanol (99.99%), 30% methanolic methylamine, and ammonium acetate (98%) were used. 3,4-Bis(2,5-dimethyl-3-thienyl)furan-2,5-dione (**I**) was synthesized by the procedure reported in [8].

Samples were irradiated with a DRSh-100 mercury lamp using light filters to isolate 313- and 546-nm lines. The electron absorption spectra were measured on a Shimadzu UV-3100 spectrophotometer. Photochromic properties of compounds **IIa-III** were studied

Scheme 3.

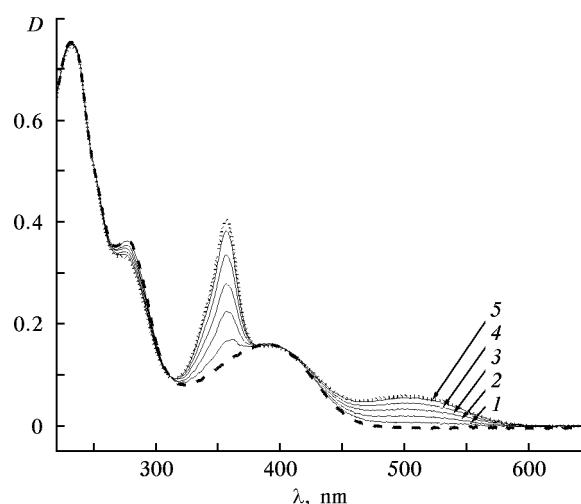


in acetonitrile. The concentration of the cyclic isomer (while studying thermal stability) was determined from the optical density at the long-wave absorption maximum of that isomer.

3,4-Bis(2,5-dimethyl-3-thienyl)pyrrole-2,5-dione (IIa). A suspension of 0.32 g (0.001 mol) of compound **I** and 0.77 g (0.01 mol) of ammonium acetate in 5 ml of anhydrous ethanol was heated for 6 h under reflux with stirring. After cooling to room temperature (20°C), the mixture was poured into ice water. The yellow powder was filtered off, washed on a filter with cold water and petroleum ether, dried over P₂O₅ under reduced pressure, and recrystallized from isopropyl alcohol. Yield 0.29 g (90%), yellow crystals with mp 196–198°C. ¹H NMR spectrum, δ, ppm: 1.89 s (6H, 5-CH₃, 5'-CH₃), 2.43 s (6H, 2-CH₃, 2'-CH₃), 6.72 s (2H, 4-H, 4'-H), 7.49 br.s (1H, NH). Mass spectrum, *m/z*: 317 [M]⁺, 302 [M-Me]⁺. Found, %: C 60.70; H 4.79; N 4.04; S 20.13. C₁₆H₁₅NO₂S₂. Calculated, %: C 60.54; H 4.76; N 4.41; S 20.20.

3,4-Bis(2,5-dimethyl-3-thienyl)-1-methylpyrrole-2,5-dione (IIb). A 5-ml portion of a 30% solution of methylamine in methanol was added with stirring to 0.32 g (0.001 mol) of compound **I**. The mixture was stirred for 36 h at ~20°C, and the needle-like crystals were filtered off, washed on a filter with cold water and petroleum ether, and dried over P₂O₅ under reduced pressure. An additional amount of the product was isolated from the filtrate by pouring it into ice water. Yield 0.28 g (85%), yellow crystals with mp 148–150°C (from methanol). ¹H NMR spectrum, δ, ppm: 1.92 s (6H, 5-CH₃, 5'-CH₃), 2.45 s (6H, 2-CH₃, 2'-CH₃), 3.13 s (3H, CH₃N), 6.71 s (2H, 4-H, 4'-H). Mass spectrum, *m/z*: 331 [M]⁺, 316 [M-Me]⁺. Found, %: C 61.52; H 5.16; N 4.54; S 18.83. C₁₇H₁₇NO₂S₂. Calculated, %: C 61.60; H 5.17; N 4.23; S 19.35.

1-Butyl-3,4-bis(2,5-dimethyl-3-thienyl)pyrrole-2,5-dione (IIc). A suspension of 0.32 g (0.001 mol) of compound **I** was added with stirring to a solution of 0.36 g (0.0049 mol) of butylamine in 5 ml of anhydrous methanol. The mixture was stirred for 1.5 h under reflux and poured into ice water. The yellow powder was filtered off, washed on a filter with cold water and petroleum ether, dried over P₂O₅ under reduced pressure, and recrystallized from isopropyl alcohol. Yield 0.27 g (73%), yellow crystals with mp 116–118°C. ¹H NMR spectrum, δ, ppm: 0.95 t (3H, CH₃), 1.40 m (2H, CH₂CH₃), 1.68 m (2H, CH₂CH₂CH₃), 1.90 s (6H, 5-CH₃, 5'-CH₃), 2.42 s (6H, 2-CH₃, 2'-CH₃), 3.60 m (2H, NCH₂), 6.72 s (2H, 4-H, 4'-H). Mass spectrum, *m/z*: 373 [M]⁺, 358



Electron absorption spectra of 3,4-bis(2,5-dimethyl-3-thienyl)-1-(2-hydroxyethyl)pyrrole-2,5-dione (**IIe**) before irradiation (dashed curve; open form **A**) and after irradiation with UV light ($\lambda = 365$ nm) for (1) 5 s, (2) 20 s, (3) 50 s, (4) 2 min, and (5) 4 min; dotted curve corresponds to the photostationary state (7 min).

[M-Me]⁺. Found, %: C 63.57; H 6.18; N 3.37; S 16.77. C₂₀H₂₃NO₂S₂. Calculated, %: C 64.31; H 6.21; N 3.75; S 17.17.

1-Benzyl-3,4-bis(2,5-dimethyl-3-thienyl)pyrrole-2,5-dione (IId) was synthesized as described above for compound **IIc** from 0.32 g (0.001 mol) of anhydride **I** and 0.54 g (0.005 mol) of benzylamine. The mixture was heated under reflux for 4 h. Yield 67%, yellow crystals with mp 193–195°C. ¹H NMR spectrum, δ, ppm: 1.86 s (6H, 5-CH₃, 5'-CH₃), 2.41 s (6H, 2-CH₃, 2'-CH₃), 4.78 s (2H, CH₂N), 6.75 s (2H, 4-H, 4'-H), 7.30–7.40 m (3H, H_{arom}), 7.41–7.51 m (2H, H_{arom}). Mass spectrum, *m/z*: 407 [M]⁺, 392 [M-Me]⁺. Found, %: C 67.28; H 5.01; N 3.01; S 14.63.

Absorption maxima of open and cyclic isomers of substituted maleimides **IIa–IIf**

Compound no.	λ_{\max} , nm	
	Isomer A	Isomer B
IIa	231, 382	357, 509
IIb	230, 276, 390	356, 500
IIc	231, 277, 389	356, 500
IId	236, 308, 389	366, 542
IIe	236, 277, 390	366, 509
IIf	231, 277, 388	357, 500

$C_{20}H_{23}NO_2S_2$. Calculated, %: C 67.78; H 5.19; N 3.44; S 15.73.

3,4-Bis(2,5-dimethyl-3-thienyl)-1-(2-hydroxyethyl)pyrrole-2,5-dione (IIe) was synthesized as described above for maleimide **IIb** from 0.32 g (0.001 mol) of compound **I** and 0.31 g (0.005 mol) of 2-aminoethanol. The mixture was stirred for 48 h. Yield 0.28 g (87%), yellow crystals with mp 122–123°C. 1H NMR spectrum, δ , ppm: 1.90 s (6H, 5-CH₃, 5'-CH₃), 2.32 br.s (1H, OH), 2.43 s (6H, 2-CH₃, 2'-CH₃), 3.85 br.s (4H, CH₂CH₂), 6.73 s (2H, 4-H, 4'-H). Mass spectrum, m/z : 361 [M]⁺, 346 [M -Me]⁺. Found, %: C 59.92; H 5.67; N 3.82; S 16.79. $C_{18}H_{19}NO_3S_2$. Calculated, %: C 59.81; H 5.30; N 3.87; S 17.74.

3,4-Bis(2,5-dimethyl-3-thienyl)-1-(6-hydroxyhexyl)pyrrole-2,5-dione (IIf) was synthesized as described above for maleimide **IId** from 0.32 g (0.001 mol) of anhydride **I** and 0.31 g (0.0022 mol) of 6-amino-1-hexanol. The mixture was refluxed for 10 h. Yield 0.31 g (75%), yellow crystals with mp 122–123°C. 1H NMR spectrum, δ , ppm: 1.90 s (6H, 5-CH₃, 5'-CH₃), 2.32 br.s (1H, OH), 2.43 s (6H, 2-CH₃, 2'-CH₃), 3.85 br.s (4H, CH₂CH₂), 6.73 s (2H, 4-H, 4'-H). Mass spectrum, m/z : 417 [M]⁺, 402 [M -Me]⁺. Found, %: C 63.08; H 6.59; N 3.32; S 15.24. $C_{22}H_{27}NO_3S_2$. Calculated, %: C 63.28; H 6.52; N 3.35; S 15.36.

REFERENCES

1. Krayushkin, M.M., Yarovenko, V.N., Shirinyan, V.Z., Semenov, S.L., Vorontsova, L.G., Starikova, Z.A., Martynkin, A.Yu., Ivanov, V.L., and Uzhinov, B.M., *Russ. J. Org. Chem.*, 2002, vol. 38, no. 9, pp. 1329–1332.
2. Dürr, H. and Bouas-Laurent, H., *Photochromism. Molecules and Systems*, Amsterdam: Elsevier, 1990.
3. Irie, M., *Chem. Rev.*, 2000, vol. 100, pp. 1685–1716.
4. Krayushkin, M.M., *Khim. Geterotsikl. Soedin.*, 2001, pp. 19–40.
5. Irie, M. and Uchida, K., *Bull. Chem. Soc. Jpn.*, 1998, vol. 71, pp. 985–996.
6. Uchida, K., Kido, Y., Yamaguchi, T., and Irie, M., *Bull. Chem. Soc. Jpn.*, 1998, vol. 71, pp. 1101–1108.
7. Nakayama, Y., Hayashi, K., and Irie, M., *J. Org. Chem.*, 1990, vol. 55, pp. 2592–2596.
8. Shirinyan, V.Z., Krayushkin, M.M., Belen'kii, L.I., Vorontsova, L.G., Starikova, Z.A., Martynkin, A.Yu., Ivanov, V.L., and Uzhinov, B.M., *Khim. Geterotsikl. Soedin.*, 2001, pp. 81–88.
9. Krayushkin, M.M., Shirinyan, V.Z., Belen'kii, L.I., Shadronov, A.Yu., Vorontsova, L.G., and Starikova, Z.A., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2002, no. 8, pp. 1392–1395.
10. Shirinian, V.Z., Belen'kii, L.I., and Krayushkin, M.M., Abstracts of Papers, *The 12th European Symp. on Organic Chemistry*, July 13–18, 2001, Groningen, The Netherlands, P. 1–166.