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

Photochromic Dihetarylethenes: XVI.* Synthesis of 1,2-Dihetarylethenes on the Basis of Thieno[3,2-*b*]pyrrole

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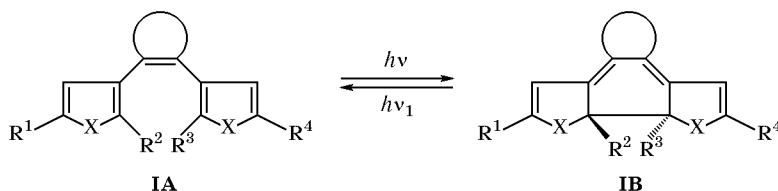
Abstract—The reaction of 3,4-dichlorocyclobutene-1,2-dione with methyl 2-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate occurs at the thiophene ring of the latter, yielding a product in which the thienopyrrole fragments are linked through a dioxocyclobutene ring. Oxidation of this product with hydrogen peroxide gives previously unknown thermally stable photochromic system containing thienopyrrole groups linked through a 2,5-dioxofuran bridge.

Thermally stable photochromic 1,2-dihetarylethenes **I**, which are characterized by a high recycling factor (the number of cycles involving reversible transformation of open form **A** into cyclic isomer **B**, which corresponds to 20% decomposition of photochromic compound [2]; Scheme 1), attract considerable interest as promising elements for optical recording systems [2, 3]. We previously showed that the recycling factor of dithienylethenes appreciably increases on introduction of heteroaromatic substituents (R^1 and R^4) into the thiophene rings [3]. It is also known that photochromic compounds on the basis of fused heterocycles (benzothiophene, indole, and thieno[3,2-*b*]thiophene) are characterized by a high recycling factor [2, 3]. As a rule, hexafluorocyclopentene, maleic anhydride, and maleimide moieties were bridging groups in such

systems. It should be emphasized that compounds in which indole rings are linked through a furandione or maleimide fragment exhibit not only photochromic properties [4] but also various kinds of biological activity and are extensively studied as promising drugs and makeup preparations [5, 6].

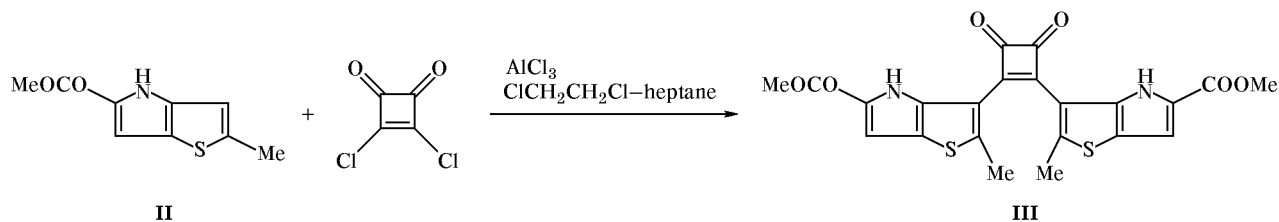
In the present work we have synthesized 1,2-dihetarylethenes containing thienopyrrole fragments, which are structurally related to the above listed groups, and examined their properties. In the preceding communications we described reactions of various thiophene derivatives with 3,4-dichlorocyclobutene-1,2-dione and proposed a general procedure for the synthesis of mono- and dithienylcyclobutenediones [1, 8, 9]. We also developed a procedure for preparation of thienopyrrole **II** and found optimal conditions

Scheme 1.

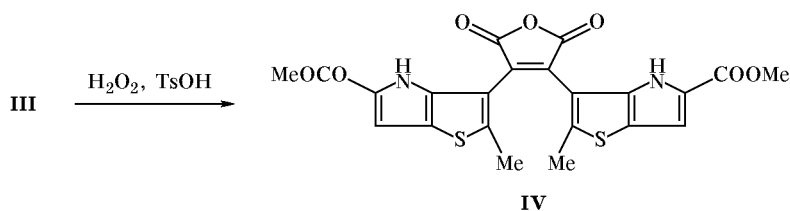


* For communication XV, see [1].

Scheme 2.



Scheme 3.



for its regioselective acylation with acetyl chloride and haloacetyl chlorides at position 3 or 6 of the heterocyclic system. Specifically, selective acylation at the thiophene ring can be effected with the use of excess AlCl_3 . The isomeric products were isolated and identified, and the NMR signals of each isomer were assigned unambiguously. In particular, addition of an acyl group to one of the heterorings changes the position of the corresponding carbon atom, whereas the chemical shift of unsubstituted carbon atom in the other heteroring remains almost unchanged [7].

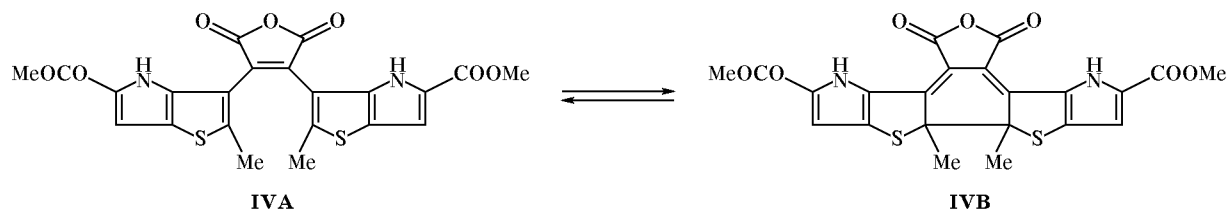
The synthesis and identification of compound **III** were performed with account taken of the above results. The reaction of 2 equiv of methyl 2-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**II**) with 1 equiv of 3,4-dichlorocyclobutene-1,2-dione was carried out in the presence of a large excess of AlCl_3 in a dichloroethane-heptane mixture. The initial thienopyrrole molecule has several reaction centers, so that the reaction could occur at positions 3, 4, and 6 to give a complex mixture of isomeric products. Nevertheless, we succeeded in isolating 3,4-bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)cyclobutene-1,2-dione (**III**) in 62% yield (Scheme 2). The structure of product **III** was con-

firmed by the data of IR and NMR spectroscopy, mass spectrometry, and elemental analysis. The mass spectrum of **III** contains the molecular ion peak with m/z 468. In the ^1H NMR spectrum we observed a singlet at δ 7.17 ppm, which belongs to the pyrrole ring proton [7]. Compound **III** shows in the ^{13}C NMR spectrum signals at δ_{C} 113.1 and 107.6 ppm. Taking into account that the signals at 110.3 and 107.4 ppm in the spectrum of initial thienopyrrole **II** belong to C^3 and C^6 , respectively [7], we concluded that the addition of cyclobutenedione fragment occurs just at the thiophene ring carbon atoms. The chemical shift of C^6 (pyrrole ring) almost does not change.

Compound **III** was oxidized with hydrogen peroxide in acetonitrile in the presence of a catalytic amount of *p*-toluenesulfonic acid. As a result, dioxofuran **IV** was obtained (Scheme 3). It showed in the ^1H NMR spectrum a singlet at δ 7.10 ppm from two pyrrole ring protons. The molecular ion peak in the mass spectrum of **IV** had an m/z value of 484.

Photochromic properties of compounds **III** and **IV** were studied in acetonitrile solution. UV irradiation of **III** induces its irreversible decomposition; therefore, this compound attracts no interest as potential photochrome. Dioxofuran derivative **IV** showed typical

Scheme 4.



photochromic properties: no appreciable decomposition was observed after at least 20 series of photo-induced transformation from open isomer **IVA** with λ_{\max} 294 nm to cyclic form **IVB** with λ_{\max} 522 nm (see figure and Scheme 4). The cyclic isomer of **IV** is stable in the dark for at least 270 h.

The overall yield of 3,4-bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)furan-2,5-dione (**IV**) is 42% (calculated on the initial thienopyrrole **II**). A conclusion may be drawn that the proposed approach to synthesis of photochromic compounds on the basis of maleic anhydride, which includes reaction of 3,4-dichlorocyclobutene-1,2-dione with thienyl derivatives and subsequent oxidation of the dioxocyclobutene ring, is general. In terms of the developed approach, such fairly promising photochromic systems have become accessible.

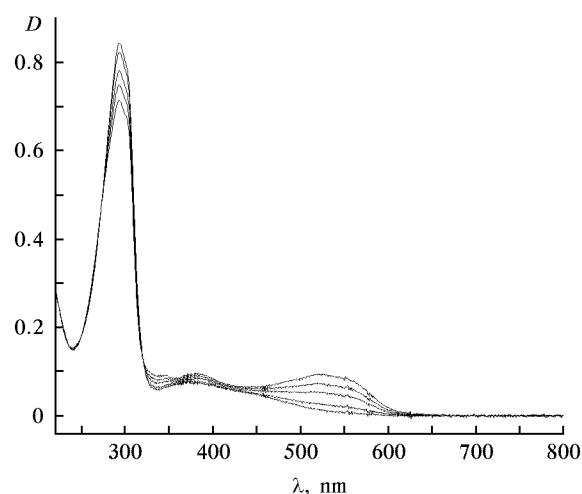
EXPERIMENTAL

The ^1H NMR spectra were recorded on Bruker WM-200 (200 MHz) and Bruker WM-250 (250 MHz) instruments in $\text{DMSO-}d_6$ using tetramethylsilane as internal reference. The mass spectra (70 eV) were obtained on a Varian MAT CH-6 spectrometer with direct admission of samples into the ion source (accelerating voltage 1.75 kV). The melting points were determined with the aid of a Boetius device and were not corrected. The reaction mixtures were analyzed, and the purity of the products was checked, by TLC on Silufol UV-254 plates using ethyl acetate-hexane (1 : 3) and ethyl acetate as eluent.

Samples were irradiated with a DRSh-100 mercury lamp through light filters to isolate 313- and 546-nm lines. The electron absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer.

Dichloroethane was dehydrated by distillation over P_2O_5 . 3,4-Dichlorobutene-1,2-dione was synthesized by the procedure described in [8].

3,4-Bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)cyclobutene-1,2-dione (III). A solution of 0.232 g (1.54 mmol) of 3,4-dichlorobutene-1,2-dione in 20 ml of dry dichloroethane was added dropwise to a suspension of 1.68 g (12.6 mmol) of aluminum chloride and 0.6 g (3.07 mmol) of methyl 2-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**II**) [7] in a mixture of 160 ml of dichloroethane and 40 ml of heptane, stirred at -10°C under argon. The mixture was allowed to warm up to 0°C , stirred for 1 h at that temperature and then for 6 h at room temperature (TLC), and poured onto ice. The organic phase was separated, the aqueous phase was treated



Variation of the electron absorption spectrum of compound **IV** on irradiation.

with methylene chloride (3×50 ml), and the extracts were combined with the organic phase, washed with a 2% solution of NaHCO_3 (2×25 ml), 25 ml of water, and 25 ml of a saturated solution of NaCl , dried over magnesium sulfate, and evaporated under reduced pressure. The residue was recrystallized from CHCl_3 -hexane (3 : 1). Yield 0.446 g (62%), mp $240\text{--}242^\circ\text{C}$ (from CHCl_3). IR spectrum (KBr), ν , cm^{-1} : 1772 s (C=O). ^1H NMR spectrum, δ , ppm: 2.20 s (6H, CH_3), 3.85 s (6H, CH_3O), 7.17 s (2H, CH), 11.35 s (2H, NH). Mass spectrum, m/z : 468 [M] $^+$. Found, %: C 56.12; H 3.45; N 5.72; S 13.48. $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_6\text{S}_2$. Calculated, %: C 56.40; H 3.44; N 5.98; S 13.69.

3,4-Bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)furan-2,5-dione (IV). A solution of 0.424 g (0.9 mmol) of 3,4-bis(5-methoxycarbonyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)cyclobutene-1,2-dione (**III**), 14 ml of 20% hydrogen peroxide, and 0.004 g (0.023 mmol) of *p*-toluenesulfonic acid in 25 ml of acetonitrile was stirred for 3 h at $65\text{--}70^\circ\text{C}$ and was left to stand overnight. The precipitate was filtered off. Yield 0.31 g (70%), mp $273\text{--}275^\circ\text{C}$ (from acetonitrile). ^1H NMR spectrum, δ , ppm: 1.83 s (6H, CH_3), 3.97 s (6H, CH_3O), 7.10 s (2H, CH), 11.82 s (2H, NH). Mass spectrum, m/z : 484 [M] $^+$. Found, %: C 56.31; H 3.43; N 5.76; S 13.18. $\text{C}_{22}\text{H}_{16}\text{N}_2\text{O}_7\text{S}_2$. Calculated, %: C 56.54; H 3.33; N 5.98; S 13.24.

REFERENCES

1. Krayushkin, M.M., Shirinyan, V.Z., Belen'kii, L.I., and Shadronov, A.Yu., *Izv. Ross. Akad. Nauk, Ser. Khim.*, 2002, no. 8, pp. 1396–1398.

2. Irie, M., *Chem. Rev.*, 2000, vol. 100, pp. 1685–1716.
3. Krayushkin, M.M., *Khim. Geterotsikl. Soedin.*, 2001, no. 1, pp. 19–40.
4. JPN Patent no. 06-161 024, 1994; *Chem. Abstr.*, 1995, vol. 122, no. 68408 g.
5. US Patent no. 5 891 901, 1999; *Chem. Abstr.*, 1999, vol. 130, no. 267 343 x.
6. WO PCT 98 11105, 1998; *Chem. Abstr.*, 1998, vol. 128, no. 257 664 x.
7. Yarovenko, V.N., Semenov, S.L., Ignatenko, A.V., Zavarzin, I.V., and Krayushkin, M.M., *Izv. Akad. Nauk, Ser. Khim.*, 2002, in press.
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, no. 37, pp. 81–88.
9. Krayushkin, M.M., Shirinyan, V.Z., Belen'kii, L.I., and Shadronov, A.Yu., *Izv. Akad. Nauk, Ser. Khim.*, 2001, no. 1, pp. 107–112.