Russian Journal of Organic Chemistry, Vol. 39, No. 11, 2003, pp. 1656–1659. Translated from Zhurnal Organicheskoi Khimii, Vol. 39, No. 11, 2003, pp. 1725–1728.

Fotochromic Dihetarylethenes: XIX.* Synthesis of 1,2-Dihetarylethenes with 2,5-Dihydrothiophene Bridge from Thieno[3,2-*b*]pyrroles

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Received December 15, 2002

Abstract—Reductive cyclization by McMurry method was performed with diketosulfide obtained by treating with Na_2S of compound prepared by regioselective acylation of methyl 2-methyl-4*H*-thieno[3,2-b]pyrrole-5-carboxylate with chloroacetyl chloride. As a result was synthesized a photochromic 1,2-dihetarylethene where the fuzed rings are connected by a 2,5-dihydrothiophene ring. The oxidation of the latter provides 2,5-dihydrothiophene-1,1-dioxide bridge.

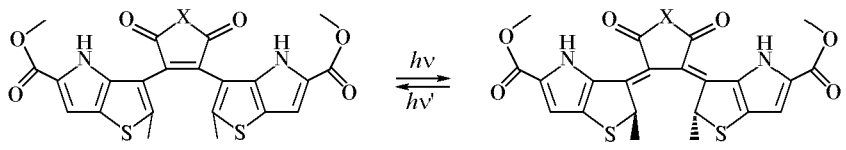
Photochromic properties of 1,2-dihetarylethenes which are now considered as promising materials for optoelectronics [2, 3] depend essentially on the character of heterocyclic compounds and bridging fragments between them. It is known that high recurrence and thermal stability is inherent to photochromic products containing fused heterocycles: benzothiophene, indol, and thieno[3,2-*b*]thiophene [3, 4]. As connecting bridges in these systems serve as a rule fragments of hexaflyorocyclopentene, maleic anhydride, and maleimide.

We were first to show recently that thieno[3,2-*b*]-pyrroles, close heterocyclic analogs of the mentioned three diheterocycles, are interesting precursors for designing thermally stable photochromic products. As connecting bridge in these substances maleic anhydride and various maleimides were applied [1, 5].

In continuation of our research on the effect of heterocycle and bridging fragment nature on the properties of photochromic compounds we report here on preparation of 1,2-dihetarylethenes containing thieno[3,2-*b*]pyrrole rings linked by 2,5-dihydrothiophene or 2,5-dihydrothiophene-1,1-dioxide rings.

In the synthesis of the target structures we used an approach described in the literature and involving a reaction of 3-chloroacetylthiophene with Na_2S followed by cyclization of the diketosulfide under conditions of McMurry reaction into dihydrothiophene ring [6, 7]. It should be noted however that in both publications the yields of products of the reductive cyclization did not exceed 11–18%. Therefore a significant goal of our study consisted also in investigation of the influence of thienopyrrole character on the stage of diketosulfide fragment cyclization affording the dihydrothiophene bridge in the 1,2-dihetarylethene.

The synthesis of the initial α-chloroketone **II** was carried out by procedure we had previously developed for regioselective acylation of methyl 2-methyl-4*H*-thieno[3,2 -*b*]pyrrole-5-carboxylate (**I**) with chloroacetyl chloride in the thiophene ring leaving intact the pyrrole ring [8]. In reaction of compound **II** with Na_2S in ethanol solution the corresponding diketosulfide **III** was obtained in 80% yield (Scheme 1).



X = O, NR.

* For communication XVIII see [1].

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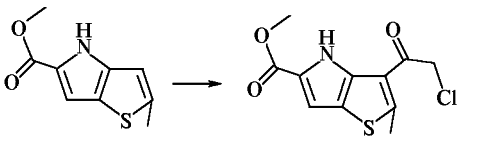
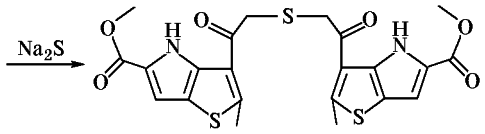
Scheme 1.

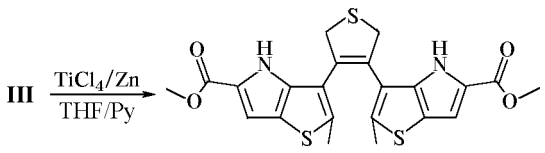


I **II**

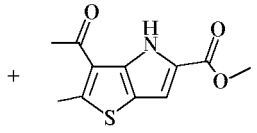


III

Scheme 2.

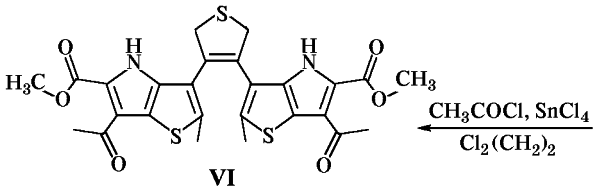


IV

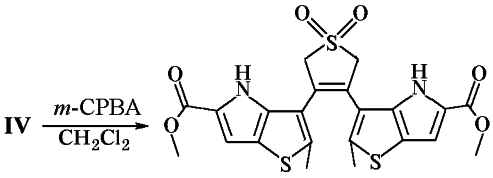


V

Scheme 3.



VI



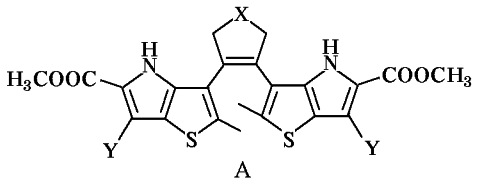
From the published data cited above followed that in the cyclization of diketosulfide fragment attached to position *3* of the thiophene ring under conditions of McMurry reaction the best yields (11–18%) of the product with a dihydrothiophene ring were obtained at the use of $TiCl_4$ and Zn in THF in the presence of pyridine [7]. In our case sulfide **III** gave rise to a mixture of 1,2-dihetarylethene **IV** and ketoester of thienopyrrole **V**. The separation of the mixture by flash-chromatography afforded photochromic compound **IV** in 51% yield (Scheme 2).

Aiming at extending the range of photochromic products we introduced acetyl groups into the *6* position of compound **IV**, and also carried out oxidation of the sulfur atom in the dihydrothiophene ring.

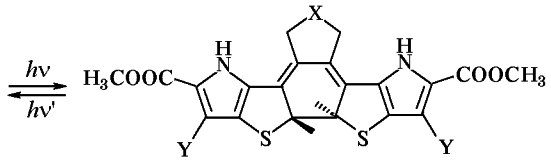
We showed formerly that it was possible to introduce cleanly an acyl group into the *6* position of thienopyrrole at the use of excess $SnCl_4$ [8]. It turned out actually that the treating of compound **IV** with two equiv of acetyl chloride in the presence of this catalyst successfully furnished photochromic product **VI** with acyl groups in both pyrrole rings (Scheme 3).

The reaction of compound **IV** with *m*-chloroperbenzoic acid (*m*-CPBA) afforded photochromic sulfone **VII** in a moderate yield.

The photochromic characteristics of compounds **IV, VI**, and **VII** were investigated in acetonitrile solution (see table, Figs. 1–3). In the absorption spectra of all compounds under study appear isobestic points, and coincidence of their positions for the direct and reverse reactions demonstrates the



A



B

Photochemical characteristics of compounds synthesized

Compd. no.	λ_{max} of open-chain form, nm	λ_{max} of cyclic form, nm	Thermal stability without irradiation
IV, X = S, Y = H	293	501, 523	200 h
VI, X = S, Y = $COCH_3$	252, 326	517	In 20 h 4% of cyclic form decomposed
VII, X = SO_2, Y = H	291	513	In 20 h 6% of cyclic form decomposed

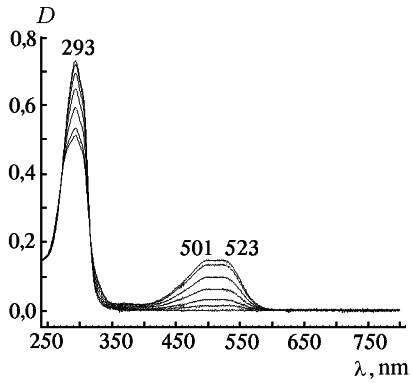


Fig. 1. Variations in the absorption spectrum of compound **IV** at irradiation with light at λ = 313 nm.

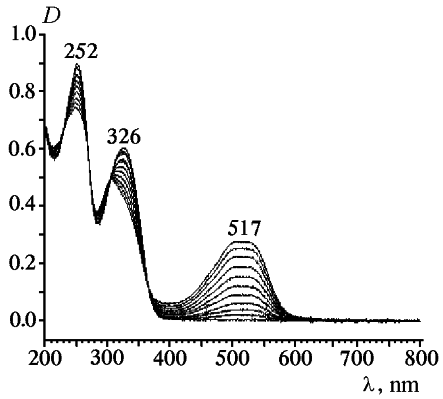


Fig. 2. Variations in the absorption spectrum of compound **VI** at irradiation with light at λ = 313 nm.

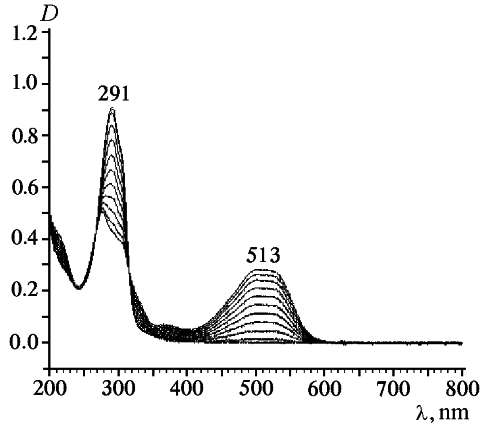


Fig. 3. Variations in the absorption spectrum of compound **VII**at irradiation with light at λ = 313 nm.

complete reversibility of photocyclization and the lack of side processes. The absorption maximum of the open-chain form of dihydrothiophene **IV** is observed in the region 293 nm; the maxima of the longwave absorption band belonging to the cyclic form B appear at 500 and 523 nm (with a fine structure). The cyclic form B of the compound is thermally stable judging from no changes in the intensity of the absorption bands within 200 h at no irradiation.

The introduction of electron-withdrawing substituents into compound **IV** both an the sulfur atom or into the pyrrole ring resulted in lower thermal stability of compounds **VI** and **VII** (see the table).

EXPERIMENTAL

^{1}H NMR spectra were registered on spectrometers Bruker WM-200 (200 MHz) and Bruker WM-250 (250 MHz) from solutions in DMSO-d_6 or $CDCl_3$, internal reference HMDS. Mass spectra were measured on Varian MAT CH-6 instrument with direct ample admission into the ion source, ionizing electrons energy 70 eV, and accelerating voltage 1.75 kV. Melting points were determined on Boetius heating block and reported without correction. Analysis of all reaction mixtures and purity checking of compounds isolated was carried out by TLC on Silufol UV-254 plates, eluent AcOEt-*n*-C_6H_{14} (1:3, by volume).

Initial methyl 3-chloroacetyl-2-methyl-4*H*-thieno-[3,2-*b*]pyrrole-5-carboxylate (**II**) was synthesized by procedure we had described before [8]. Anhydrous 1,2-dichloroethane and dichloromethane were obtained by distillation from P_2O_5. The samples were irradiated by a mercury lamp DRSh-100 using light filters to isolate mercury spectrum lines of 313 and 546 nm. The absorption spectra were registered on spectrophotometer Shimadzu UV-3100.

Bis[2-(2-methyl-5-methoxycarbonyl-4*H*-thieno-[3,2-*b*]pyrrol-3-yl)-2-oxoethyl] sulfide (III). To 1.2 g (4.42 mmol) of α-chloroketone **II** in 35 ml of EtOH was added 0.53 g (2.21 mmol) of $Na_2S{\cdot}9H_2O$ in 10 ml of water. The reaction mixture was heated at reflux for 30 min. The precipitate was filtered off, washed with hot EtOH, and dried in air. We obtained 0.87 g (78%) of compound **III**, mp 202–204°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 2.74 s (6H, $2CH_3$), 3.85 s (6H, $2CH_3O$), 4.18 s (4H, $2CH_2$), 7.13 s (2H, 2CH arom), 11.32 s (2H, 2NH). Mass spectrum, *m/z*: 504 $[M]^+$. Found, %: C 52.43; H 4.00; N 5.62; S 19.15. $C_{22}H_{20}N_2O_6S_3$. Calculated, %: C 52.37; H 3.99; N 5.55; S 19.06.

3,4-Bis-(2-methyl-5-methoxycarbonyl-4*H*-thieno-[3,2-*b*]pyrrol-3-yl)-2,5-dihydrothiophene (IV). To a vigorously stirred suspension of 0.311 g (4.76 mmol) of zinc in 20 ml of freshly distilled

anhydrous THF cooled to –10°C under argon atmosphere was added dropwise through a syringe 0.26 ml (2.38 mmol) of $TiCl_4$. After completion of addition the reaction mixture was heated in the argon atmosphere for 1 h, then cooled to 20°C, and 0.2 ml of anhydrous pyridine and 0.6 g (1.19 mmol) of dioxosulfide **III** was cautiously added thereto. The reaction mixture was heated to boiling under argon for 6 h more, and then poured into 50 ml of 10% K_2CO_3 solution. The water layer was extracted with ethyl ether (3 × 40 ml), the combined organic solutions were dried over $MgSO_4$, and the solvent was distilled off in a vacuum. The pure reaction product was isolated by flash-chromatography on silica gel (Merck, 0.063–0.1), eluent petroleum ether (bp 40–70°C)–AcOEt (4 : 1 by volume). We obtained 0.28 g (51%) of compound **IV**, mp 141–143°C ($CHCl_3$-*n*-C_6H_{14}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.16 s (6H, $2CH_3$), 3.83 s (6H, $2CH_3O$), 4.25 s (4H, $2CH_2$), 6.97 s (2H, 2CH arom), 9.13 s (2H, 2NH). Mass spectrum, *m/z*: 472 $[M]^+$. Found, %: C 56.05; H 4.30; N 6.03; S 20.55. $C_{22}H_{20}N_2O_4S_3$. Calculated, %: C 55.91; H 4.27; N 5.93; S 20.35.

Also was separated 0.12 g (21%) of methyl 3-acetyl-2-methyl-4*H*-thieno[3,2-*b*]pyrrole-5-carboxylate (**V**), mp 167–169°C (from EtOH) (publ.: 168–170°C [8]). Mass spectrum, *m/z*: 237 $[M]^+$. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.58 s (3H, CH_3), 2.82 s [3H, $CH_3C(O)$], 3.90 s (3H, CH_3O), 7.02 s (1H, CH), 9.84 br.s (1H, NH). Found, %: C 55.73; H 4.66; N 6.12; S 13.72. $C_{13}H_{13}NO_4S$. Calculated, %: C 55.68; H 4.67; N 5.90; S 13.51.

3,4-Bis-(2-methyl-5-methoxycarbonyl-6-acetyl-4*H*-thieno[3,2-*b*]pyrrol-3-yl)-2,5-dihydrothiophene (VI). To 0.06 g (0.13 mmol) of dihydrothiophene **IV**, 0.06 ml (0.54 mmol) of $SnCl_4$ in 2 ml of dichloroethane was added 0.02 ml (0.28 mmol) of acetyl chloride. The reaction mixture was stirred for 15 h, then poured in water, extracted with dichloromethane (2 × 20 ml), the extract was washed with saturated aqueous NaCl, and dried over $MgSO_4$. The solvent was removed in a vacuum. The residue was recrystallized from a mixture CH_2Cl_2-*n*-C_6H_{14} (1 : 1, by volume). We obtained 0.05 g (71%) of compound **VI**, mp 131–133°C (from CH_2Cl_2-*n*-C_6H_{14}). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.31 s (6H, $2CH_3$), 2.69 s (6H, $2CH_3CO$), 3.84 s (6H, $2CH_3O$), 4.21 s (4H, $2CH_2$), 9.20 s (2H, 2NH). Mass spectrum, *m/z*: 556 $[M]^+$. Found, %: C 56.30; H 4.34; N 5.17; S 17.40. $C_{26}H_{24}N_2O_6S_3$. Calculated, %: C 56.10; H 4.35; N 5.03; S 17.28.

3,4-Bis-(2-methyl-5-methoxycarbonyl-4*H*-thieno-[3,2-*b*]pyrrol-3-yl)-2,5-dihydrothiophene-1,1-dioxide (VII). To 0.1 g (0.21 mmol) of dihydrothiophene **IV** in 10 ml of anhydrous CH_2Cl_2 at 0–5°C while stirring was added dropwise 0.103 g (0.6 mmol) of *m*-CPBA in 10 ml of anhydrous CH_2Cl_2. The reaction mixture was stirred for 1 h at 0–5°C and 12 h at 25°C, then poured in water, the organic layer was separated, and the water layer was extracted with $CHCl_3$ (2 × 20 ml). The combined organic solutions were washed with water (2 × 20 ml) and dried over $MgSO_4$. The solvent was removed in a vacuum. The pure product was isolated by preparative chromatography on silica gel. We obtained 0.02 g (19%) of compound **VII**, mp 228–230°C (from $CHCl_3$). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.24 s (6H, $2CH_3$), 3.82 s (6H, $2CH_3O$), 4.53 s (4H, $2CH_2$), 6.93 s (2H, 2CH arom), 10.57 s (2H, 2NH). Mass spectrum, *m/z*: 504 $[M]^+$. Found, %: C 52.40; H 4.00; N 5.61; S 19.20. $C_{22}H_{20}N_2O_6S_3$. Calculated, %: C 52.37; H 3.99; N 5.55; S 19.06.

The study was carried out under financial support of ISTC (grant no. 2117).

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