1208 *Russian Chemical Bulletin, International Edition, Vol. 54, No. 5, pp. 1208—1213, May, 2005*

# Synthesis and photochromic properties of tetrakis(3,5-dimethyl-2-thienyl)- and tetrakis(2,5-dimethyl-3-thienyl)ethylenes*

***L. I. Belen´kii,* G. P. Gromova, A. V. Kolotaev, B. V. Nabatov, and M. M. Krayushkin***

*N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,*
*47 Leninsky prosp., 119991 Moscow, Russian Federation.*
*Fax: +7 (095) 135 5328. E-mail: libel@ioc.ac.ru*

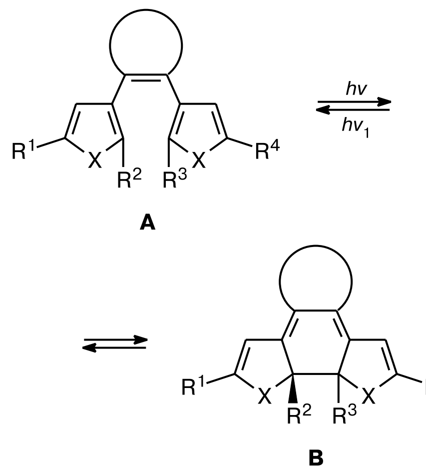
Tetrakis(3,5-dimethyl-2-thienyl)ethylene and tetrakis(2,5-dimethyl-3-thienyl)ethylene were obtained from the corresponding dithienyl ketones by the McMurry reaction. The photochromic properties of the compounds obtained were studied.

**Key words:** dihetarylethenes, photochromes, McMurry reaction, thiophenes, ketones.

Photochromic compounds and materials are capable of being transformed reversibly, so that substance **A** (photochrome) exposed to light is converted into product **B**, which differs from **A** in absorption spectrum (color) and other physicochemical properties. Photochromes are used in actinometers, dosimeters, various optoelectronic devices, and such common goods as sun glasses; presently, they are considered to be extremely promising systems for data storage.[1]

The possibility of using photochromes as optical storage elements is determined first of all by two specific properties: the number of the interconversions **A** $\rightleftarrows$ **B** until 20% of a sample has decomposed[2] (fatigue resistance) and the thermal irreversibility of phototransformations. 1,2-Dihetarylethenes are ones of the best thermally irreversible photochromes, their fatigue resistance being high (up to 10 000 cycles).[3] Since only *cis*-1,2-dihetarylethenes are capable of photocyclization of the desired type, *cis-trans* isomerization must be prevented. This is attained by fixing the *cis*-form in cyclic ethene fragments (most often, these are the residues of perfluorocyclopentene, maleic anhydride, and maleimide) (Scheme 1).[1,2]

**Scheme 1**



At the same time, it is evident that if tri- or tetrasubstituted ethylene contains three or four identical hetaryl residues, its *cis-trans* isomerization is degenerate and such compounds retain the ability to photocyclize. In the present work, we describe the syntheses of tetrakis(3,5-dimethyl-2-thienyl)ethylene (**1**) and tetrakis(2,5-dimethyl-3-thienyl)ethylene (**2**) and the primary data on their photochromic properties.

Compounds **1** and **2** were obtained from the corresponding ketones **3** and **4** by the McMurry reaction (Scheme 2). The starting ketones were prepared by sequential reactions: formylation of dimethylthiophenes **5** and **6**, oxidation of aldehydes **7** and **8** into acids **9** and **10**, their transformation into acid chlorides, and final acylation of dimethylthiophenes **5** and **6**.

The McMurry reaction, which is a reductive coupling of carbonyl compounds in the presence of low-valence titanium reagents (see reviews[4,5]), has been repeatedly used to synthesize photochromic dithienylethenes with perfluorocyclopentene and cycloalkene fragments[6,7] and 2,5-dihydrothiophene as the ethene bridge.[8,9] Nonphotochromic tetra(2-thienyl)ethylene has also been obtained by this reaction.[10] However, for the syntheses of the target compounds **1** and **2**, thorough optimization of the reaction conditions was required.

The reduction of bis(3,5-dimethyl-2-thienyl) ketone (**3**) with a low-valence titanium reagent generated in the $TiCl_4$—Zn system led to tetrakis(3,5-dimethyl-2-

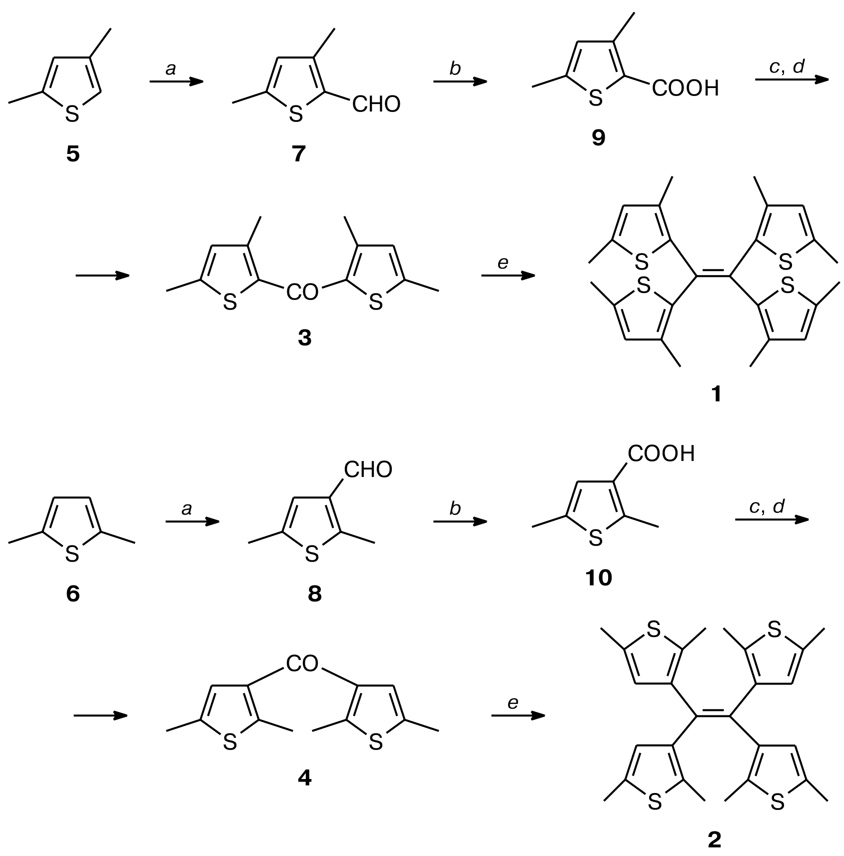
---

* Dedicated to the Academician N. K. Kochetkov on the occasion of his 90th birthday.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 1177—1181, May, 2005.

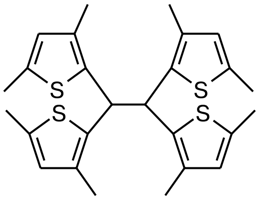
1066-5285/05/5405-1208 © 2005 Springer Science+Business Media, Inc.

**Scheme 2**

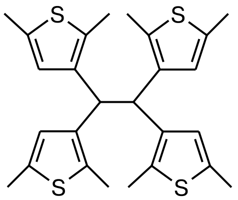


**Reagents and conditions:** *a*. $Me_2NCHO/POCl_3$ (in the synthesis of compound **1**) or $MeOCHCl_2/TiCl_4$ (in the synthesis of compound **2**); *b*. $CrO_3$, $H_2SO_4$, acetone; *c*. $SOCl_2$; *d*. 2,4-dimethylthiophene (in the synthesis of compound **1**) or 2,5-dimethylthiophene (in the synthesis of compound **2**), $AlCl_3$, $CH_2Cl_2$; *e*. $TiCl_3$—$LiAlH_4$.

thienyl)ethane (**11**) in 65% yield. When starting from bis(2,5-dimethyl-3-thienyl) ketone (**4**), we obtained a mixture of ethylene **2** and tetrakis(2,5-dimethyl-3-thienyl)ethane (**12**) in the nearly 1 : 1 ratio; the overall yield of these compounds was 40%.



**11**



**12**

It is worth noting that the intramolecular McMurry reaction with the same system afforded 3,4-bis(2,5-dimethyl-3-thienyl)-2,5-dihydrothiophene only in 11% yield[8,9] (no other products were mentioned). Earlier,[11] an attempted cyclization of 2,4-dimethyl-2,4-bis(2,5-dimethyl-3-thenoyl)-3-thiapentane under the same conditions gave no 3,4-bis(2,5-dimethyl-3-thienyl)-2,2,5,5-tetramethyl-2,5-dihydrothiophene as the expected product of the McMurry reaction; instead, this compound underwent reductive desulfurization leading to 3-isobutyroyl-2,5-dimethylthiophene. When a titanium reagent was generated in the $TiCl_3$—$LiAlH_4$ system, a mixture of a desulfurization product and 3,4-bis(2,5-dimethyl-3-thienyl)-2,2,5,5-tetramethyl-2,3,4,5-tetrahydrothiophene was obtained; however, no formation of the target dihydrothiophene derivative was observed.

The use of the $TiCl_3$—$LiAlH_4$ system for generation of a low-valence titanium reagent for ketones **3** and **4** yielded mixtures **1** + **11** and **2** + **12** in the 3 : 1 and 6 : 1 ratios, respectively. The target products, namely, tetrakis(3,5-dimethyl-2-thienyl)ethylene (**1**) and tetrakis(2,5-dimethyl-3-thienyl)ethylene (**2**), were isolated from the reaction mixtures. The structures of substituted ethylenes **1** and **2** and substituted ethanes **11** and **12** were confirmed by $^1H$ NMR and mass spectra and elemental analysis data. In particular, the $^1H$ NMR spectrum of compound **1** agrees with the published data for its close analogs, namely, tetra(2-thienyl)ethylene and its derivatives

**Table 1.** Photochromic and fluorescent properties of solutions of compounds **1** and **2** in acetonitrile ($c = 1 \cdot 10^{-4}$ mol L$^{-1}$)

| Compound | $\lambda_A$/nm | $D_A$ | $\lambda_B$/nm | $D_B$ | $\lambda^A{}_{Fl}$/nm | $I^A{}_{Fl}$ /rel. unit | $\Delta\lambda$/nm |
|---|---|---|---|---|---|---|---|
| **1** | 255 | 1.71 | 255 | 1.76 | 330 | 0.75 | 42 |
| | 288 | 1.72 | 288 | 1.55 | 530 | 0.2 | 148 |
| | 382 | 1.12 | 382 | 0.89 | | | |
| **2** | 314 | 0.81 | 313 | 1.02 | 400 | 0.95 | 86 |
| | | | 451 | 0.14 | | | |

*Note*. The exposure time was 3 min.

tetra(5-methyl-2-thienyl)- and tetra(5-methylthio-2-thienyl)ethylenes.[10]

We estimated the photochromic and fluorescent properties of compounds **1** and **2**. The results obtained are given in Table 1.

When compound **1** was alternately irradiated with light at wavelengths of 365 and 313 nm, no new absorption bands appeared in the visible range; the position and shape of the persistent absorption band at $\lambda = 382$ nm remained unchanged, although its optical density decreased or increased in proportion to the irradiation duration and the light wavelength. Simultaneously, opposite changes were observed in the UV range from 250 to 290 nm (Fig. 1, *a*). Note that after an irradiated sample of compound **1** was kept in the dark for 10 days, its optical densities at $\lambda = 382$ and 250—290 nm changed noticeably, approaching the initial (preirradiation) values. Compound **1** fluoresces (two emission bands at $\lambda^A{}_{Fl} = 330$ and 530 nm). Compound **2** exhibits both photochromic (the closed form with an absorption maximum at 450 nm (Fig. 2, *b*)) and fluorescent properties (the band at 400 nm).

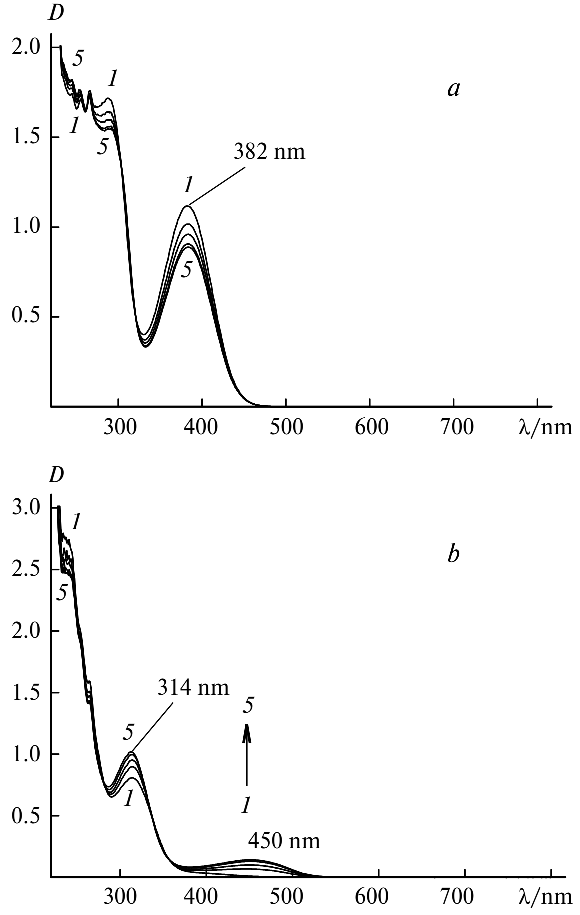
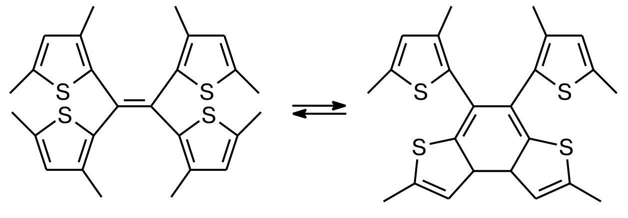
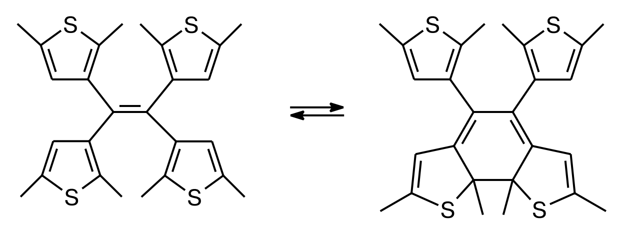


**Fig. 1.** Electronic absorption spectra of solutions of compounds **1** (*a*) and **2** (*b*) in acetonitrile at 298 K for a 1-cm-thick layer: (*1*) the initial solutions; (*2*)—(*5*) the solutions exposed to light with $\lambda = 365$ (for **1**) or 313 nm (for **2**) for 0.5 (*2*), 1 (*3*), 2 (*4*), and 3 min (*5*).

Thus, with tetrathienylethylene **2** as an example, we discovered a route to photochromic systems of this type. The behavior of compound **1** calls for further discussion. Earlier,[12] it was found that the electronic absorption spectrum of *N*-cyanomethyl-2,3-bis(3,4-dimethyl-5-phenyl-2-thienyl)maleimide, which also contains the 2-thienyl fragments, remained unchanged upon irradiation with visible and UV light at any wavelength. This was associated[12] with the inefficiency of photocyclization and a high quantum yield of ring opening. Apparently, compound **1** is a



**1A** **1B**



**2A** **2B**

thermally reversible inverse photochrome, in which cyclic form **1B** provides less efficient conjugation (di(vinylthio)butadiene fragment C=C—S—C=C—C=C—S—C=C) than open form **1A** (decapentaene fragment C=C—C=C—C=C—C=C—C=C).

At the same time, in the photochromic transformation of tetra(β-thienyl)ethylene **2A**, the di(vinylthio)hexatriene fragment C=C—S—C=C—C=C—C=C—S—C=C changes into the octatetraene fragment C=C—C=C—C=C—C=C in cyclic form **2B**. It is also possible that the formation of a new C—C bond in the transformation **1A** → **1B** requires more energy *h*ν than that transferred during the irradiation with this (minimum possible) wavelength.

## Experimental

$^1$H NMR spectra were recorded on Bruker AM-300 and Bruker AC-200 instruments in $CDCl_3$. Mass spectra (EI) were recorded on a Kratos instrument (70 eV, direct inlet probe). Melting points were determined on a Boetius microscope stage and are given uncorrected. The course of the reactions was monitored and the purity of the products was checked by TLC on Silica gel 60 $F_{254}$ plates (Merck); spots were visualized under UV light). Column chromatography was carried out on $SiO_2$-60 silica gel (0.060—0.200 mm; Merck).

Titanium tetrachloride, zinc powder (high-purity grade), lithium aluminum hydride, titanium trichloride, and α,α-dichlorodimethyl ether (Aldrich Co.) were used. Acetonitrile (99% purity, Acros Co.) was employed for spectroscopic measurements.

The absorption and fluorescence spectra of solutions of compounds **1** and **2** irradiated with visible and UV light were recorded on a Varian Cary 50 Bio spectrophotometer and a Fluorat-02 Panorama spectrofluorimeter using an OI-18A luminescent illuminator fitted with a DRK-120 mercury quartz lamp. The concentrations of compounds **1** and **2** in acetonitrile were $1 \cdot 10^{-4}$ mol $L^{-1}$. Measurements were carried out in 10-mm quartz cuvettes under the following conditions: monochromator step 1 nm, slit width 3 nm, and averaging over three to five points in each step. The results obtained are given in Table 1.

The initial solution of compound **1** at the aforesaid concentration is colored pale yellow with a greenish tinge. This solution was alternately (alternation was effected every 4 min) irradiated through light filters for λ = 365 and 313 nm and its absorption spectra were recorded. The color of the irradiated solution remained virtually unchanged.

The fluorescence spectra of compound **1** were recorded before irradiation of its solution by scanning the emission wavelength range for two excitation wavelengths: $\lambda^{Ex}{}_1 = 300$ nm and $\lambda^{Ex}{}_2 = 380$ nm. The spectra contained two fluorescence bands with the emission maxima at 330 and 530 nm.

The initial solution of compound **2** was transparent in the visible range of the spectrum. The irradiated solution turned pale yellow because of the formation of cyclic form **2B** with the absorption maximum $\lambda^{B}{}_{max} = 450$ nm. Irradiation of the solution at the wavelength of this new band caused the cyclic form to undergo opening, the solution becoming colorless. Such a closure—opening cycle was repeated several times to check the photochromic properties of this compound.

The fluorescence spectra of compound **2** were recorded as described for compound **1**. Excitation of the initial solution with light at $\lambda^{Ex} = 340$ nm resulted in its luminescence at 400 nm.

**2,4-Dimethylthiophene (5)** was prepared according to a known procedure[13] by the Kishner—Wolff reduction of 2,4-thiophenedicarbaldehyde.[14]

**2,5-Dimethylthiophene (6)** was prepared as described earlier[15] from acetonylacetone and phosphorus pentasulfide.

**3,5-Dimethylthiophene-2-carbaldehyde (7).** Phosphorus oxychloride (5.1 mL, 8.54 g, 55.8 mmol) was added at 10 °C to DMF (9.7 g, 132.8 mmol). The resulting complex was kept at 75—80 °C for 10 min and cooled to 10 °C and 2,4-dimethylthiophene (5 g, 44.6 mmol) was added. The resulting brown solution was heated at 70—75 °C for 3 h and cooled to ~20 °C. The thick mixture was decomposed with 15% $CH_3COONa$ (aq, 30 mL). The product was extracted with chloroform (5×30 mL), washed with water, and dried over $MgSO_4$. The solvent was distilled off to give aldehyde **7** (4.15 g, 66%), b.p. 120 °C (15 Torr), which agrees with the literature data.[16]

**2,5-Dimethylthiophene-3-carbaldehyde (8).** Solutions of α,α-dichlorodimethyl ether (7.3 g, 90.6 mmol) in $CH_2Cl_2$ (15 mL) and 2,5-dimethylthiophene (7.8 g, 69.6 mmol) in $CH_2Cl_2$ (15 mL) were added simultaneously from two funnels at $T \leq 5$ °C to a solution of $TiCl_4$ (33.1 g, 19.1 mL, 174 mmol) in $CH_2Cl_2$ (20 mL). The mixture was kept at this temperature for 2 h (until the evolution of HCl was ceased), warmed to room temperature over 30 min, poured into ice acidified with HCl, washed with water, and dried over $MgSO_4$. The solvent was removed and the residue was distilled to give aldehyde **8** (5.85 g, 60%), b.p. 114 °C (20 Torr), which agrees with the literature data.[17]

**3,5-Dimethylthiophene-2-carboxylic acid (9).** The Jones reagent (12 mL) prepared from $CrO_3$ (39 g), water (117 mL), and conc. $H_2SO_4$ (30 mL) was added to a stirred solution of aldehyde **7** (1.8 g, 12.9 mmol) in acetone (40 mL) cooled in a water bath (≤20 °C). The addition rate was regulated so that the orange color disappeared. The mixture was stirred at room temperature for 6 h. The solution was decanted from the green precipitate of $Cr_2O_3$ and concentrated to ~1/10 of the volume and the precipitate was washed with ether. The ethereal extract was combined with the concentrated solution in acetone and washed with water to remove sulfuric acid. Acid **9** was extracted with a saturated solution of $NaHCO_3$. Acidification with conc. HCl gave acid **9** (0.86 g), m.p. 170—173 °C, which agrees with the literature data.[16] The ethereal extract was concentrated and the residue (0.6 g) containing the starting aldehyde was reoxidized with the Jones reagent to give an additional crop of acid **9** (0.25 g). Its total yield was 1.11 g (~55%).

**2,5-Dimethylthiophene-3-carboxylic acid (10)** was obtained as described for acid **9**. The yield of compound **10** was 65%, m.p. 114—115 °C, which agrees with the literature data.[18]

**3,5-Dimethylthiophene-2-carbonyl chloride** was obtained by the action of thionyl chloride (1.24 g, 0.75 mL) on acid **9** (1.47 g, 9.4 mmol) in the presence of a catalytic amount of DMF. The mixture was stirred at room temperature for 3 h, $SOCl_2$ was removed, and the residue was distilled. The yield of the acid chloride was 1.85 g (62.5%), b.p. 97 °C (2.5 Torr). The product was used without additional purification.

**2,5-Dimethylthiophene-3-carbonyl chloride** was obtained analogously from acid **10** in 65% yield.

**Bis(3,5-dimethyl-2-thienyl) ketone (3).** Aluminum trichloride (0.68 g, 5.1 mmol) was added in portions to a stirred solution of the chloride (0.8 g, 4.58 mmol) obtained from acid **9** and 2,4-dimethylthiophene (**5**) (0.52 g, 4.68 mmol) in $CH_2Cl_2$ (10 mL). The mixture was kept for 4 h and poured into water. The product was extracted with $CH_2Cl_2$ and the extract was dried over $MgSO_4$. The solvent was removed and the residue was recrystallized from hexane. The yield of compound **3** was 72%, m.p. 60 °C. Found (%): C, 62.26; H, 6.19; S, 25.05. $C_{13}H_{14}OS_2$. Calculated (%): C, 62.36; H, 5.64; S, 25.61.

**Bis(2,5-dimethyl-3-thienyl) ketone (4)** was obtained analogously from 2,5-dimethylthiophene (**6**). The yield of compound **4** was 85%, m.p. 65 °C, which agrees with the literature data.[18]

**McMurry condensation of bis(3,5-dimethyl-2-thienyl) ketone (3).** ***A.*** Titanium tetrachloride (0.63 g, 3.3 mmol) was added dropwise in an atmosphere of argon at $T \leq 5$ °C to dry THF (10 mL). Then a Zn powder (0.425 g, 6.6 mmol) and a solution of ketone **3** (0.55 g, 2.2 mmol) in THF (6 mL) were added in portions. The resulting black mixture was kept at $T \leq 5$ °C for 2 h and dry pyridine (0.2 mL) was added. The mixture was refluxed to decoloration (10 h) and treated with a solution of $K_2CO_3$ (2 g) in water (20 mL). The inorganic precipitate that formed was filtered off and washed with ether. The organic products from the aqueous solution were extracted with ether. The combined ethereal extracts were dried over $MgSO_4$ and concentrated.

**Tetrakis(3,5-dimethyl-2-thienyl)ethane (11)** was precipitated by addition of several milliliters of hexane to the residue. The yield of compound **11** was 0.34 g (65%), m.p. 207—210 °C (from hexane). Found (%): C, 66.19; H, 6.47; S, 26.68. $C_{26}H_{30}S_4$. Calculated (%): C, 66.33; H, 6.42; S, 27.24. $^1$H NMR, δ: 1.99 (s, 12 H, 4 Me); 2.31 (s, 12 H, 4 Me); 4.91 (s, 2 H, 2 $H_{ethane}$); 6.27 (s, 4 H, $H_{thioph}$). MS, $m/z$ ($I_{rel}$ (%)): 235 $[M/2]^+$ (100).

***B.*** Titanium trichloride (0.36 g, 2.4 mmol) and $LiAlH_4$ (0.045 g, 1.2 mmol) were added successively in an atmosphere of argon to cooled dry THF (8 mL). The resulting mixture was refluxed to the formation of a reductive black mixture (30 min). The mixture was cooled and ketone **3** (0.3 g, 1.2 mmol) in dry THF (2 mL) was added. The mixture was kept at ~20 °C for 15 min and refluxed to decoloration (6.5 h). Tetrahydrofuran (15 mL) and ether (15 mL) were added and the mixture was poured into water (10 mL). The precipitate that formed was filtered off, the organic layer was separated, and the products from the aqueous layer were extracted with ether. The combined extracts were washed with water, dried over $MgSO_4$, and concentrated. The residue was additionally purified on silica gel with light petroleum—ethyl acetate (100 : 1) as an eluent. The eluent was removed to give a mixture of compounds **1** and **11** in the ratio 4.5 : 1 ($^1$H NMR data). The overall yield was 0.27 g (70%).

**Tetrakis(3,5-dimethyl-2-thienyl)ethylene (1)** was isolated by washing the above mixture with hexane; m.p. 170—173 °C. Found (%): C, 66.42; H, 6.13; S, 27.05. $C_{26}H_{28}S_4$. Calculated (%): C, 66.62; H, 6.02; S, 27.35. $^1$H NMR, δ: 1.80 (s, 12 H, 4 Me); 2.35 (s, 12 H, 4 Me); 6.35 (s, 4 H, $H_{thioph}$). MS, $m/z$ ($I_{rel}$ (%)): 468 $[M]^+$ (27), 235 $[M/2+H]^+$ (100).

**McMurry condensation of bis(2,5-dimethyl-3-thienyl) ketone (4).** ***A.*** A mixture of ketone **4** (0.25 g, 1 mmol), $TiCl_4$ (0.2 g, 1.05 mmol), a Zn powder (0.15 g, 2.25 mmol), and pyridine (0.086 mL) in dry THF (5 mL) was refluxed under argon for 7 h. The resulting thick mass was treated with 10% $K_2CO_3$ (50 mL) and the products were extracted with $CH_2Cl_2$. The extract was washed with water, dried over $MgSO_4$, and concentrated. Benzene (3 mL) was added to the residue and a substance (0.04 g) with m.p. 230—248 °C was separated. According to $^1$H NMR data, the substance was tetrakis(2,5-dimethyl-3-thienyl)ethane (**12**) with an admixture of ethene **2**. The benzene solution was concentrated to an oil, from which a substance (0.05 g) with m.p. ~200 °C was precipitated with hexane. According to $^1$H NMR data, the substance was tetrakis(2,5-dimethyl-3-thienyl)ethylene (**2**) with an admixture of ethane **12**. The overall yield of compounds **2** and **12** was ~40%.

***B.*** A mixture of $TiCl_3$ (0.25 g, 1.6 mmol), $LiAlH_4$ (0.03 g, 0.8 mmol), and ketone **4** (0.2 g, 0.8 mmol) in dry THF (8 mL) was prepared as described for ketone **3** (procedure ***B***). The mixture was refluxed for 7.5 h and treated with THF (5 mL), ether (5 mL), and water (10 mL). The organic layer was separated and the products from the aqueous layer were extracted with ether. The extract was washed with water, dried over $MgSO_4$, and concentrated to an oil containing compounds **2** and **12** in the ratio 6 : 1 ($^1$H NMR data). A solid was isolated by addition of hexane (3 mL); the solid was ethylene **2** (90% purity; $^1$H NMR data). The residue was separated by column chromatography with light petroleum—ethyl acetate (50 : 1) as an eluent to give additional crops of ethylene **2** (0.02 g) and ethane **12** (~0.02 g). The total yield of compound **2** was 0.11 g (58%).

**Tetrakis(2,5-dimethyl-3-thienyl)ethylene (2)** was isolated by washing the above mixture with hexane; m.p. 198 °C. Found (%): C, 66.27; H, 6.14; S, 27.43. $C_{26}H_{28}S_4$. Calculated (%): C, 66.62; H, 6.02; S, 27.35. $^1$H NMR, δ: 1.89 (s, 12 H, 4 Me); 2.24 (s, 12 H, 4 Me); 6.15 (s, 4 H, $H_{thioph}$). MS, $m/z$ ($I_{rel}$ (%)): 468 $[M]^+$ (33), 235 $[M/2+H]^+$ (100).

**Tetrakis(2,5-dimethyl-3-thienyl)ethane (12)** was isolated by chromatography; m.p. 247—250 °C. Found (%): C, 66.15; H, 6.54; S, 26.91. $C_{26}H_{30}S_4$. Calculated (%): C, 66.33; H, 6.42; S, 27.24. $^1$H NMR, δ: 2.08 (s, 12 H, 4 Me); 2.25 (s, 12 H, 4 Me); 4.31 (s, 2 H, 2 $H_{ethane}$); 6.47 (s, 4 H, $H_{thioph}$). MS, $m/z$: 235 $[M/2]^+$.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32878) and the International Scientific and Technical Center (Project No. 2117).

## References

1. M. M. Krayushkin, *Khim. Geterotsikl. Soedin.*, 2001, 19 [*Chem. Heterocycl. Compd.*, 2001 (Engl. Transl.)].
2. M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
3. M. Irie and M. Mohri, *J. Org. Chem.*, 1988, **53**, 803.
4. J. E. McMurry, *Acc. Chem. Res.*, 1983, **16**, 405.
5. D. Lenoir, *Synthesis*, 1989, 883.
6. L. N. Lucas, J. van Esch, R. M. Kellogg, and B. L. Feringa, *Chem. Commun.*, 1998, 2313.
7. L. N. Lucas, J. van Esch, R. M. Kellogg, and B. L. Feringa, *Tetrahedron Lett.*, 1999, **40**, 1775.

8. B. A. Xu, Z. N. Huang, S. Jin, Y. F. Ming, M. G. Fan, and S. D. Yao, *J. Photochem. Photobiol. A: Chem.*, 1997, **110**, 35.
9. Z. N. Huang, B. A. Xu, S. Jin, and M. G. Fan, *Synthesis*, 1998, 1092.
10. T. Suzuki, H. Shiohara, M. Monobe, T. Sakimura, Sh. Tanaka, Y. Yamashita, and Ts. Miyashi, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 455.
11. L. I. Belen´kii, G. P. Gromova, A. V. Kolotaev, and M. M. Krayushkin, *Karbonil´nye soedineniya v sinteze geterotsiklov* [*Carbonyl Compounds in Heterocyclic Synthesis*], Nauchnaya Kniga, Saratov, 2004, p. 34 (in Russian).
12. K. Uchida, Y. Kido, T. Yamaguchi, and M. Irie, *Bull. Chem. Soc. Jpn*, 1998, **71**, 1101.
13. L. I. Belen´kii and A. P. Yakubov, *Tetrahedron*, 1984, **40**, 2471.
14. I. B. Karmanova, Yu. B. Vol´kenshtein, and L. I. Belen´kii, *Khim. Geterotsikl. Soedin.*, 1973, 490 [*Chem. Heterocycl. Compd.*, 1973 (Engl. Transl.)].
15. S. N. Ivanov, B. V. Lichitskii, A. A. Dudinov, A. Yu. Martynkin, and M. M. Krayushkin, *Khim. Geterotsikl. Soedin.*, 2001, 890 [*Chem. Heterocycl. Compd.*, 2001 (Engl. Transl.)].
16. J. Sicé, *J. Org. Chem.*, 1954, **19**, 70.
17. A. P. Glaze, S. A. Harris, H. G. Heller, W. Johncock, S. Oliver, P. J. Strydom, and J. Whittall, *J. Chem. Soc., Perkin Trans. 1*, 1985, 957.
18. N. P. Buu-Hoi and Nguyen-Hoan, *Rec. Trav. Chim.*, 1948, **67**, 309.

*Received March 25, 2005;*
*in revised form April 5, 2005*