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A NEW APPROACH TO THE SYNTHESIS OF DITHIENYLETHANEDIONES AND DITHIENYLACETYLENES*

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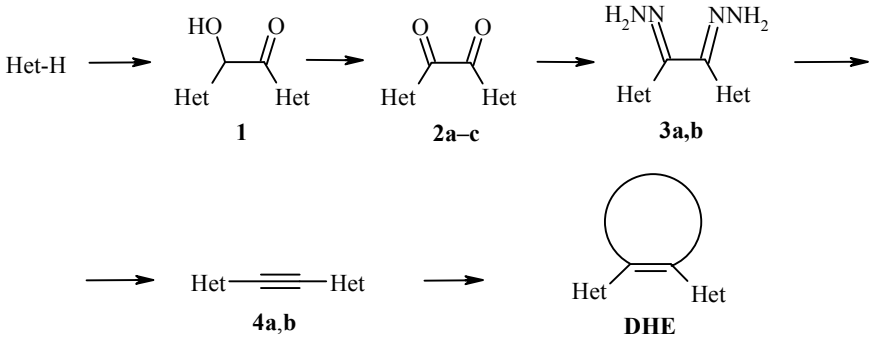
1,2-Dithienylethanediones were synthesized by modified acylation of thiophene and its homologs in the presence of aluminum chloride and pyridine. The bishydrazones of the products were converted into dithienylacetylenes by oxidation with atmospheric oxygen in pyridine in the presence of CuCl.

Keywords: Friedel–Crafts acylation, dithienylacetylenes, 1,2-dithienylethanediones, oxalyl chloride, pyridine, thiophenes, thiophenium ions, aluminum chloride.

In connection with investigations into the synthesis of photochromic dithienylethenes with new ethene bridges (see the review [4]) we have proposed a strategy whose main feature is the formation of the *cis*-dihetarylethene (DHE) system from dihetarylacetylene (Scheme 1). The scheme includes the production of thenoins **1**, their oxidation to α-diketones **2**, conversion of the diketones into the osazones **3**, and oxidation of the latter to the acetylenes **4**.

Scheme 1



2-4 a Het = 2,5-dimethyl-3-thienyl, **b** Het = 3,5-methyl-2-thienyl, **2c** Het = 5-methyl-2-thienyl

* Parts of the content of this paper have been published in a letter to the editor [1] and in abstracts [2, 3]. Dedicated to J. Stradins on his 70th birthday with deep respect and great affection.

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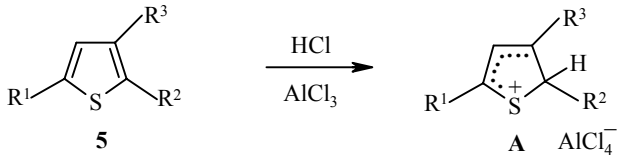
In the present work we set out the results relating to the synthesis of dithienylacetylenes of type **4**. Oxidation of the bishydrazones of the respective α-diketones, which is a process well-known in the production of diarylacetylenes, had not previously been used in the thiophene series, while dithienylacetylenes were synthesized almost exclusively by the condensation of halothiophenes with acetylene and its derivatives catalyzed by palladium compounds (e.g., see [5, 6]). In view of the general aim of the investigation, as model product we selected bis(2,5-dimethyl-3-thienyl)acetylene (**4a**), and the intended synthesis path seemed extremely reasonable since both the final dithienylacetylenes **4** and the intermediate thenoins **1** and α-diketones **2** could be used as potential precursors of photochromic dithienylethenes. It should be noted here that several examples both of benzoin condensation and of the oxidation of thenoins to the respective α-diketones have been described (see, particularly, [7]).

However, we were unable to obtain the thenoin **1a** either from 2,5-dimethyl-3-thiophenecarbaldehyde under the classical conditions of benzoin condensation (KCN in ethanol [8] or under conditions of modified reaction from the respective Schiff base (KCN in DMSO [9]). The products from the benzoin condensation of β-thiophenecarbaldehydes are usually formed with low yields, while in the investigated case this reaction may be further complicated by steric hindrances on account of the presence of the methyl group at position 2*. Subsequently, therefore, we concentrated our efforts on the synthesis of diketones of type **2** by acylation of the thiophene homologs 2,5-dimethylthiophene (**5a**), 2,4-dimethylthiophene (**5b**), and 2-methylthiophene (**5c**) with oxalyl chloride.

Acylation of dimethylthiophene **5a** under the standard conditions of the Friedel–Crafts reaction [in 1,2-dichloroethane (DCE) in the presence of aluminum chloride] led to the diketone **2a**, but its yield was not greater than 18%. In addition to side products, 20-25% of the initial dimethylthiophene was recovered.

In our opinion one of the reasons for the low yields of the acylation products was the formation of a σ-complex of type **A** (Scheme 2). As mentioned in [13], during the acylation of activated compounds of the thiophene series in the presence of aluminum chloride the hydrogen chloride formed in the process is not released from the reaction medium but protonates the initial thiophene compound, forming an amount of a σ-complex of type **A** that is approximately equimolar in relation to the acylation product. During standard treatment of the reaction mixture the complex is converted into the initial thiophene.

Scheme 2



5 **A** $AlCl_4^-$

a $R^1 = R^2 = Me$, $R^3 = H$, **b** $R^1 = R^3 = Me$, $R^2 = H$, **c** $R^1 = Me$, $R^2 = R^3 = H$

If $SnCl_4$ is used as condensing agent, the reaction goes to completion on account possibly of the low stability of the σ-complex, and recovery of the initial thiophene is not observed [13, 14]. It is, however, necessary to emphasize that in the presence of this catalyst even at high temperatures (80-100°C) compounds of

* It should be noted that more recently in our laboratory the thenoin **1a** was synthesized according to a scheme including oxidation of the methyl ketone with selenium dioxide and condensation of the obtained keto aldehyde with a thiophene compound [10], and the diketone **2a** was synthesized by its oxidation [11]. Compounds **1a** and **2a** were transformed into a series of heterocycles containing two adjacent 2,5-dimethyl-3-thienyl substituents, and some of the latter had photochromic characteristics [11, 12].

the thiophene series are not acylated by acid chlorides containing electron-withdrawing substituents such as chloroacetyl chloride [1, 15], oxalyl chloride [1], and squaric dichloride [1], and the initial thiophene is recovered almost completely. In such cases it is necessary to use a stronger Lewis acid ($AlCl_3$), which unfortunately leads at the same time to the undesirable formation of a relatively stable complex of type **A** and reduces the yield of the final product.

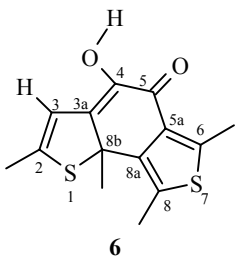
Earlier we proposed a modified method for the acylation of compounds of the thiophene series in the presence of aluminum chloride and pyridine as an acceptor of the HCl that destroys the above-mentioned σ-complex, creating the possibility of increasing the yield of the desired products [1]. In the present work we studied the effect of these conditions on the acylation of the thiophene homologs **5a-c** by oxalyl chloride and showed that the use of pyridine makes it possible to suppress the formation of the σ-complexes **A** and to increase the yields of the α-diketones **2a-c** to 45-60%. The composition and structure of the products were confirmed by elemental analysis and NMR spectra. However, additions of pyridine do not prevent the formation of the side products.

In the case of dimethylthiophene **5a** it was possible to isolate and identify two products. To judge from the results of elemental analysis and the NMR spectra, which are discussed below, one of them (compound **6**) is an isomer of the desired 1,2-bis(2,5-dimethyl-3-thienyl)ethanedione (**2a**), while the other (product **7**) is obtained from three molecules of compound **5a** and one molecule of oxalyl chloride.

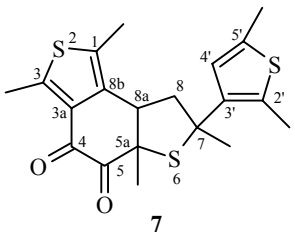
Since the NMR spectra of compounds **6** and **7** are fairly complicated and it was not possible to grow crystals suitable for X-ray crystallographic analysis, a full assignment of the signals in the ^1H and ^{13}C NMR spectra was made on the basis of joint analysis of all the one-dimensional and two-dimensional spectra, including examination of the ^1H and ^{13}C SSC data in the HMBC spectra and the coupling of the protons through space in the NOESY spectra with the use of two-dimensional heterocorrelation experiments.

In the ^{13}C NMR spectrum of compound **6** two groups of signals correspond to the methyl substituents; in the region of 13.4-18.0 (2-CH_3, 6-CH_3, 8-CH_3) and at 36.9 ppm (8b-CH_3). The presence of correlation between the 8-CH_3 and 8b-CH_3 groups in the NOESY spectrum demonstrates their proximity, which agrees with the structure of 4-hydroxy-2,6,8,8b-tetramethyl-5,8b-dihydrobenzodi[2,1-*b*:3,4-*c*]thiophen-5-one (**6**) given below. The IR spectrum (in chloroform) contains bands at 3428 (OH) and 1612 cm^{-1} (C=O), the position of which does not change on dilution, indicating the presence of an intramolecular hydrogen bond O–H···O=C.

In the ^1H NMR spectrum of compound **7** there are two groups of signals for the methyl protons: Four singlets in the region of 2.3-2.8 ppm (1-CH_3, 3-CH_3, 2'-CH_3, 5'-CH_3) and two almost completely overlapping singlets (5-CH_3 and 7-CH_3) at 1.55 ppm. In the ^{13}C NMR spectrum there are four signals in the region of 12.7-15.9 and two at 24.6 and 31.5 ppm. According to these data four methyl groups are linked to the heterocycles, while the other two are in the aliphatic part of the molecule. The three protons at 3.62, 3.01, and 2.01 ppm form an AMX spin system; it follows from the data of the COSY and HSQC spectra that they are at positions 8 (2H) and 8a (1H). On account of the overlap of the signals for the protons of the 5a-CH_3 and 7-CH_3 groups it was impossible to determine their stereochemical arrangement (*cis* or *trans*) in relation to the 8a-H proton. The presented data agree with structure of 7-(2',5'-dimethyl-3'-thienyl)-1,3,5a,7-tetramethyl-4,5,5a,7,8,8a-hexahydrobenzo[1,2-*c*;3,4-*b*]dithiophene-4,5-dione (**7**).



6



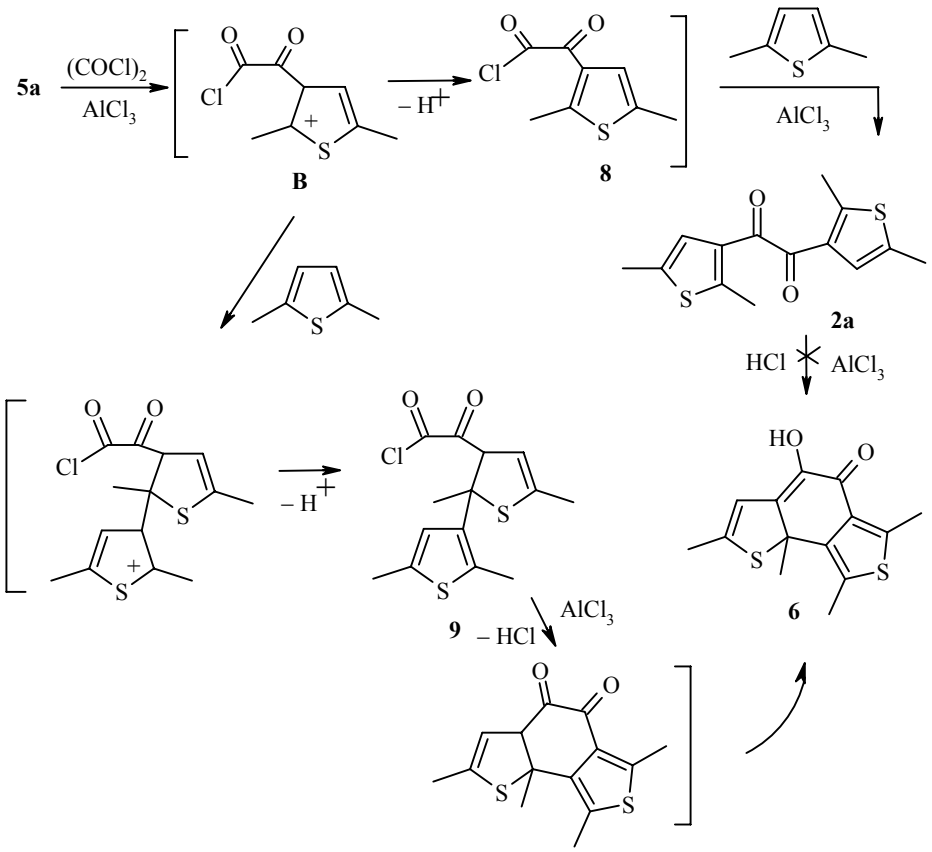
7

Probable paths for the formation of compounds **2a**, **6**, and **7** are shown in Schemes 3 and 4. Attack by the active complex of oxalyl chloride with $AlCl_3$ can be directed at the free β position or at the α position substituted by a methyl group in the molecule of dimethylthiophene **5a**, leading respectively to the σ-complexes **B** (Scheme 3) and **C** (Scheme 4). Compounds **2a** and **6** are formed from the thiophenium ion **B**, and compound **7** from the ion **C**.

The acid chloride is obtained from the ion **B** during protonation and then acylates a second molecule of the dimethylthiophene **5a** with the formation of the required product **2a**. In the anomalous process the ion **B** acts as alkylating agent, leading to the acid chloride **9**, which undergoes cyclization to compound **6**. We note that the diketone **2a** is not transformed into its isomer **6** in the presence of aluminum chloride and hydrochloric acid (Scheme 3).

It can be supposed that attack by the dimethylthiophene **5a** at position 2 of the molecule leads to the formation of the σ-complex **C**, the reaction of which with a second molecule of the dimethylthiophene **5a** leads to the acid chloride **10**. The latter undergoes cyclization to the diketone **11**, which is protonated at the β position of the dihydrothiophene fragment and is converted into the cationic reagent **12** that "alkylates" the dimethylthiophene **5a** with the formation of the anomalous product **7** (Scheme 4). If a weaker Lewis acid ($TiCl_4$) is used, the yields of the diketone and the side products **6** and **7** remain almost unchanged.

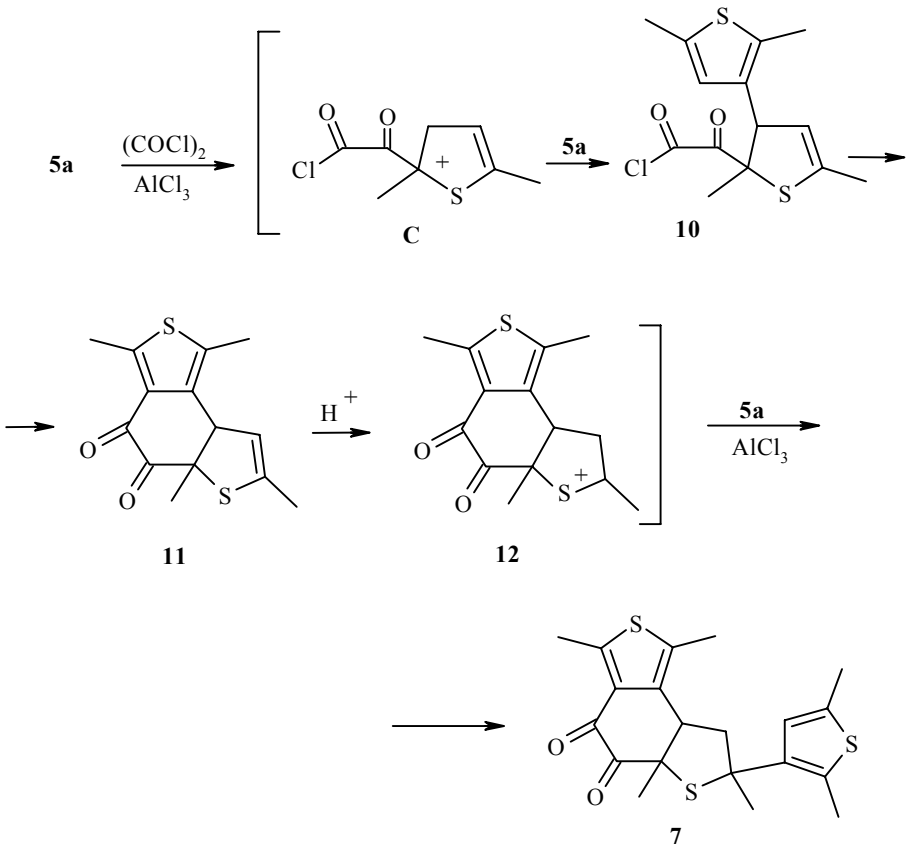
Scheme 3



Under analogous conditions – in the presence of aluminum chloride and dichloroethane – the acylation of dimethylthiophene **5b** was accompanied by significant resin formation. In order to suppress the side processes an attempt was made the reduce the polarity of the solvent in order to prevent the formation of the

σ-complex **A** and side products like compounds **6** and **7**. Decrease in the polarity of the medium leads to a decrease in the solvation energy and therefore to an increase of the activation barriers of the reactions. When a mixture of dichloroethane and heptane was used the yield of compound **2a** from dimethylthiophene **5a** was reduced, which can be explained by competing acylation at positions 2 and 3. On the other hand, with dimethylthiophene **5b** on account of the presence of the free position 2 only the diketone **2b** is formed smoothly. The proposed modification of the Friedel–Crafts acylation by strong acylating agents in the case of squaric dichloride was used successfully in our laboratory [16, 17].

Scheme 4



The dithienylethanediols **2** are then converted into the bishydrazones **3**, and the reaction takes place in two stages; in the first the monohydrazone is formed (without acid catalysis it is formed exclusively), and in the second it is transformed into the bishydrazone (osazone), which is a slower reaction than the first. In the case of bis(3,5-dimethyl-2-thienyl)ethane-1,2-dione **2b** on account evidently of steric hindrances the second stage takes place much more slowly than for its isomer **2a** (in 50 h against 11 h in the case of the diketone **2a**). The osazones **3** are readily oxidized by atmospheric oxygen (oxygen is used according to the procedure in [18]) in the presence of CuCl in pyridine solution and are converted into the corresponding dithienylacetylenes **4**.

EXPERIMENTAL

The ^{1}H NMR spectra were recorded on Bruker AC-200, WM-250, and AM-300 instruments in deuterochloroform or in DMSO-d_6 [in the case of the bishydrazones (**3a**, **b**)] with reference to the signal of the solvent. The chemical shifts are given on the δ scale with reference to TMS. During determination of the

structure of compound **7** the ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 instrument (500 and 125 MHz respectively). The two-dimensional HSQC, HMBC, and NOESY experiments were conducted by the standard Bruker procedures. The mixing time in the NOESY experiment was 1 sec. The IR spectra of compound **6** were obtained on a Specord-80 spectrometer for solutions in chloroform (concentrations ~100, 5, and 3 mM). The EI mass spectra were recorded on a Kratos instrument with direction injection of the sample into the ion source and ionization energy 70 eV.

The products from the acylation of 2-methyl- and 2,5-dimethylthiophene were separated by chromatography on a column (diameter 2 cm, height 30 cm) filled with ~80 ml of Merck silica gel (0.063-0.200 mesh) with 20:1 (a), 15:1 (b), and 10:1 (c) mixtures of petroleum ether (bp 40-70°C) and ethyl acetate as eluent. The melting points were determined on a Kofler bench and were not corrected.

Acylation of 2-Methylthiophene (5c). To a solution of aluminum chloride (3.34 g, 25 mmol) in 1,2-DCE (10 ml) at about -20°C we added dropwise in succession a solution of oxalyl chloride (0.71 g, 5.6 mmol) in DCE (5 ml), a solution of 2-methylthiophene **5c** (1.2 g, 12.2 mmol), and pyridine (0.88 g, 11 mmol) in DCE (5 ml). The mixture was kept at -20°C for 10 min, the temperature was raised to 0°C, and the mixture was poured onto ice. The products were extracted with methylene chloride, and the extract was washed to a neutral reaction with water and dried over magnesium sulfate. The residue after distillation of the solvent (1.7 g of an oil containing crystals) was purified by column chromatography (eluant a), and 0.83 g (59.4%) of di(5-methyl-2-thienyl)ethane-1,2-dione (**2c**) was obtained; mp 80-82 (mp 86-87°C [18]). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.60 (6H, s, $2CH_3$); 6.87 (2H, d, *J* ~ 4, 4-H and 4'-H); 7.86 (2H, d, *J* ~ 4, 3-H and 3'-H).

Acylation of 2,5-Dimethylthiophene (5a). A. To a suspension of aluminum chloride (1.19 g, 8.9 mmol) in 1,2-DCE (5 ml) at -20°C we added pyridine (0.36 ml) in DCE (5 ml) and then dimethylthiophene **5a** (1 g, 8.9 mmol) in DCE (5 ml). To the obtained mixture over 40 min at the same temperature we added dropwise oxalyl chloride (0.68 g, 5.35 mmol) in DCE (5 ml). The temperature of the reaction mixture was raised to 5°C over 70 min, and the mixture was poured onto ice. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layer and the extract were washed with water, sodium carbonate solution, and water to a neutral reaction and dried over magnesium sulfate. After evaporating the chloroform we obtained 1.01 g of a viscous oil, from which by column chromatography (eluant c) we isolated in succession 0.56 g of the diketone **2a** (yield on the thiophene **5a** 47%), 0.09 g (75%) of the product **6**, 0.10 g (7.5%) of compound **7**, and 0.28 g of an unidentified mixture (the residue after evaporation of the last eluate).

1,2-Bis(2,5-dimethyl-3-thienyl)ethanedione (2a). Mp 64.5-65.5°C. ^{1}H NMR spectrum, δ, ppm: 2.38 (6H, s, $2CH_3$); 2.73 (6H, s, $2CH_3$); 6.92 (2H, s, $2H_{Het}$). Found, %: C 60.55; H 5.20; S 22.71. $C_{14}H_{14}O_2S_2$. Calculated, %: C 60.40; H 5.07; S 23.03.

4-Hydroxy-2,6,8,8b-tetramethyl-5,8b-dihydrobenzo[2,1-*b*:3,4-*c*]dithiophen-5-one (6). Mp 123-124°C. IR spectrum (chloroform), ν, cm^{-1}: 3428 (OH), 1612 (C=O). ^{1}H NMR spectrum, δ, ppm: 1.82 (3H, s, 8b-CH_3); 2.19 (3H, s, 2-CH_3); 2.43 (3H, s, 8-CH_3); 2.74 (3H, s, 6-CH_3); 6.31 (1H, s, 3-H); 6.85 (1H, s, OH). ^{13}C NMR spectrum, δ, ppm: 13.43 (8-CH_3); 15.39 (6-CH_3); 18.02 (2-CH_3); 36.87 (8b-CH_3); 58.88 ($C_{(8b)}$); 115.65 ($C_{(3)}$); 127.61 ($C_{(6)}$); 129.66 ($C_{(8)}$); 138.82 ($C_{(8a)}$); 140.33 ($C_{(2)}$); 143.40 ($C_{(3a)}$); 146.96 ($C_{(5a)}$); 150.63 ($C_{(4)}$); 177.71 (CO). Found, %: C 60.16; H 5.02; S 22.21. $[M]^{+}$ 278. $C_{14}H_{14}O_2S_2$. Calculated, %: C 60.40; H 5.07; S 23.03. M 278.39.

7-(2',5'-Dimethyl-3'-thienyl)-1,3,5a,7-tetramethyl-4,5,5a,7,8,8a-hexahydrobenzo[1,2-*c*:3,4-*b*]-dithiophen-4,5-dione (7). Mp 160-162°C (benzene). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.55 (6H, s, 5a-CH_3 and 7-CH_3); 2.03 (1H, dd, ^{2}J = 13.4, $^{3}J_1$ = 11.1, 8-H_A); 2.36 (3H, s, 5'-CH_3); 2.38 (3H, s, 1-CH_3); 2.42 (3H, s, 2'-CH_3); 2.75 (3H, s, 3-CH_3); 3.01 (1H, dd, ^{2}J = 13.4, $^{3}J_2$ = 4.9, 8-H_M); 3.62 (1H, dd, $^{3}J_2$ = 11.1, $^{3}J_1$ = 4.9, 8a-H_X); 6.74 (1H, s, 4'-H). ^{13}C NMR spectrum, δ, ppm: 12.48 (1-CH_3); 14.88 (5'-CH_3); 15.15 (2'-CH_3); 15.59 (3-CH_3); 24.45 (5a-CH_3); 31.17 (7-CH_3); 50.12 ($C_{(8)}$); 52.71 ($C_{(8a)}$); 56.60 ($C_{(7)}$); 65.43 ($C_{(5a)}$); 124.82 ($C_{(4')}$); 130.90 ($C_{(1)}$); 131.22 ($C_{(2')}$); 131.60 ($C_{(3a)}$); 134.12 ($C_{(5')}$); 134.60 ($C_{(8b)}$); 142.10 ($C_{(3')}$); 152.10 ($C_{(3)}$); 177.40

($C_{(4)}$=O); 195.73 ($C_{(5)}$=O). Found, %: C 61.52; H 5.83; S 24.21. $[M]^+$ 390. $C_{20}H_{22}O_2S_3$. Calculated, %: C 61.50; H 5.68; S 24.63. M 390.59.

B. To a suspension of aluminum chloride (1.19 g, 8.9 mmol) in heptane (2 ml) at -20°C we added dimethylthiophene **5a** (1 g, 8.9 mmol) in heptene (2 ml) and then dropwise (over 40 min) oxalyl chloride (0.68 g, 5.35 mmol) in heptane (5 ml). The temperature was raised to -10°C over 10 min. The mixture was stirred at this temperature for 4 h 42 min and kept at -18°C for ~15 h. We then added 5 ml of DCE to the reaction mixture and stirred the mixture for 50 min at -10°C. The temperature was raised to -5°C over 20 min, and the mixture was stirred at this temperature for 40 min, and kept at -1°C for 3 h 30 min and at -18°C for ~15 h. It was then poured onto ice and treated as described in method A, and 1.18 g of a viscous oil was obtained. From the latter by column chromatography (eluant c) we isolated 0.35 g of the diketone **2a** (yield on the thiophene **5a** 30%), 0.39 g of a mixture of products, 0.20 g (15%) of compound **7**, and 0.24 g of a residue.

B. To a stirred solution of oxalyl chloride (0.68 g, 5.35 mmol) and $TiCl_4$ (1.69 g, 8.9 mmol) in DCE (10 ml) at a temperature between -25°C and -30°C over 1 h 12 min we added dimethylthiophene **5a** (1 g, 8.9 mmol). The claret-red reaction mixture was stirred for 1 h 20 min at -21°C to -23°C, and the temperature was then raised to -4°C. The mixture was stirred at this temperature for 20 min, poured onto ice, and treated by method A. We obtained 1.04 g of a dark oil, from which by column chromatography (eluants a, b, and c in succession) we isolated 0.54 g of the diketone **2a** (yield on the thiophene **5a** 47%), 0.03 g (2.5%) of the isomer **6**, 0.09 g of a mixture of products, 0.12 g (9%) of compound **7**, and 0.26 g of a residue.

Acylation of 2,4-Dimethylthiophene (5b). To a suspension of aluminum chloride (3.32 g, 24.9 mmol) in heptane (10 ml) at a temperature between -20 and -30°C we added in succession 2,4-dimethylthiophene (1.40 g, 12.48 mmol) in heptane (5 ml), DCE (10 ml), and oxalyl chloride (0.95 g, 7.49 mmol) in heptane (10 ml). The mixture was stirred at -20°C for 2 h 18 min, poured onto ice, and treated by method A. The residue after evaporation of the chloroform was recrystallized from alcohol, and 0.77 g (44%) of the diketone **2b** was obtained; mp 150-151°C. ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.51 (6H, s, 5- and 5'-CH_3); 2.54 (6H, s, 3- and 3'-CH_3); 6.72 (2H, s, 4- and 4'-H). ^{13}C NMR spectrum, δ, ppm: 15.80 (5- and 5'-CH_3); 17.39 (3- and 3'-CH_3); 127.97 ($C_{(5)}$); 131.35 ($C_{(4)}$); 150.74 ($C_{(2)}$); 151.82 ($C_{(3)}$); 184.06 (C=O). Found, %: C 60.38; H 4.96; S 22.29. $C_{14}H_{14}O_2S_2$. Calculated, %: C 60.40; H 5.07; S 23.03.

1,2-Bis(2,5-dimethyl-3-thienyl)ethanedione Bishydrazone (3a). To a solution of the diketone **2a** (4.97 g, 17.9 mmol) in ethanol (40 ml) we added successively hydrazine hydrate (8.94 g, 179 mmol) and a catalytic amount of TsOH. The mixture was boiled for 11 h, and the precipitate was then filtered off, washed with cold water, and dried in air. We obtained 3.33 g (60.8%) of the osazone **3a**; mp 202-204°C. ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.17 (6H, s, 5- and 5'-CH_3); 2.38 (6H, s, 2- and 2'-CH_3); 6.04 (4H, br. s, $2NH_2$); 6.45 (2H, s, 4- and 4'-H). ^{13}C NMR spectrum, δ, ppm: 14.07 (CH_3); 5.32 (CH_3); 125.43 ($C_{(4)}$); 128.43 ($C_{(2)}$); 135.40 ($C_{(3)}$); 137.49 ($C_{(5)}$); 146.08 (N=C–C=N). Found, %: C 55.01; H 6.14; N 17.95; S 20.63. $C_{14}H_{18}N_4S_2$. Calculated, %: C 54.87; H 5.92; N 18.28; S 20.93.

1,2-Bis(3,5-dimethyl-2-thienyl)ethanedione Bishydrazone (3b). To a solution of the diketone **2b** (0.80 g, 2.87 mmol) in ethanol (10 ml) we added in succession hydrazine hydrate (1.15 g, 23 mmol) and a catalytic amount of TsOH. The mixture was boiled for 30 h, hydrazine hydrate (0.51 g) was added, and the mixture was boiled for a further 20 h. The precipitate that separated after cooling was filtered off, washed with cold water, and dried in air. We obtained 0.49 g (55%) of the osazone **3b**; mp 214-216°C (from a ~1:1 mixture of alcohol and benzene). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 1.94 (6H, s, 5- and 5'-CH_3); 2.42 (6H, s, 3- and 3'-CH_3); 6.35 (4H, br. s, $2NH_2$); 6.68 (2H, s, 4- and 4'-H). ^{13}C NMR spectrum δ, ppm: 13.59 (2 CH_3); 14.68 (2 Me); 126.18 ($C_{(4)}$ and $C_{(4')}$); 129.71 ($C_{(3)}$ and $C_{(3')}$); 133.41 ($C_{(5)}$ and $C_{(5')}$); 135.39 ($C_{(2)}$ and $C_{(2')}$); 142.90 (N=C–C=N). Found, %: C 55.14; H 6.13. $C_{14}H_{18}N_4S_2$. Calculated, %: C 54.87; H 5.92.

1,2 Bis(2,5-dimethyl-3-thienyl)acetylene (4a). A stream of dry air was passed through a vigorously stirred suspension of copper(I) chloride (2.15 g, 21.7 mmol) in anhydrous pyridine (20 ml) for 1 h, after which a solution of the bishydrazone **3a** (3.33 g, 10.9 mmol) in dry pyridine (35 ml) was added in four portions. (Each

successive portion was added after the brown color of the reaction mixture had changed to green.) The mixture was stirred at room temperature for 2 h in a stream of dry air and kept at the same temperature for 16 h. The pyridine was then evaporated, and a 2 N solution of hydrochloric acid (64 ml) was added. The aqueous solution was extracted with ether (6 × 5 ml), and the extract was washed successively with water, saturated solutions of sodium bicarbonate and sodium chloride, and again with water to a neutral reaction and dried over magnesium sulfate. The residue after evaporation (2.55 g) was recrystallized from ethanol, and 2.16 g (80.7%) of the product **4a** was obtained; mp 66-67°C (ethanol). ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.43 (6H, s, 2- and 2'-CH_3); 2.53 (6H, s, 5- and 5'-CH_3); 6.69 (2H, s, 4- and 4'-H). ^{13}C NMR spectrum, δ, ppm: 14.46 (2 CH_3); 15.22 (2 CH_3); 86.06 (C≡C); 119.63 ($C_{(2)}$ and $C_{(2')}$); 127.21 ($C_{(4)}$ and $C_{(4')}$); 135.72 ($C_{(5)}$ and $C_{(5')}$); 140.55 ($C_{(3)}$ and $C_{(3')}$). Found, %: C 68.28; H 5.86; S 25.32. $[M]^+$ 246. $C_{14}H_{14}S_2$. Calculated, %: C 68.25; H 5.73; S 26.03. M = 246.40.

1,2-Bis(3,5-dimethyl-2-thienyl)acetylene (4b). The compound was obtained in the same way as compound **4a** from 0.20 g of the bishydrazone **3b**. The yield of the product **4b** after crystallization from ethanol was 86.6%; mp 62-64°C. ^{1}H NMR spectrum, δ, ppm, *J* (Hz): 2.28 (6H, s, 2- and 2'-CH_3); 2.44 (6H, s, 5- and 5'-CH_3); 6.53 (2H, s, 4- and 4'-H). ^{13}C NMR spectrum, δ, ppm: 15.15 (2 CH_3); 15.46 (2 CH_3); 87.66 (C≡C); 116.34 ($C_{(5)}$ and $C_{(5')}$); 127.81 ($C_{(4)}$ and $C_{(4')}$); 140.45 ($C_{(2)}$ and $C_{(2')}$); 142.48 ($C_{(3)}$ and $C_{(3')}$). Found, %: C 67.78; H 5.58; S 25.88. $C_{14}H_{14}S_2$. Calculated, %: C 68.25; H 5.73; S 26.03.

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