Chemistry of Heterocyclic Compounds, Vol. 44, No. 9, 2008

REACTIONS OF 2,5-DI(2-THIENYL)PYRROLES*

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We have studied the possible modification of 2,5-di(thienyl)pyrroles with the aim of preparing compounds which can serve as precursors of polymers and monomers showing electrical conductivity and specific photochemical properties.

Keywords: 3-acetyl-2,5-di(thienyl)pyrroles, 2,5-di(thienyl)pyrrole-3-carbaldehydes, 2,5-di(thienyl)-pyrroles, 3-hydroxymethyl-2,5-di(thienyl)pyrroles, acetylation, O-alkylation, intermolecular C-alkylation, formylation, reduction.

2,5-Di(2-thienyl)pyrroles consist of thiophene and pyrrole rings interconnected by their α-positions and are undoubtedly of interest in the preparation from them of electroconductive materials ("organic metals"), in particular as components of organic light-emitting diodes (see, for example, the reviews [1-6]. The extremely high reactivity of a pyrrole system creates the possibility of introducing a substituent into the β-position of the pyrrole ring even with the free α-positions of thiophene rings which makes possible further modification of the properties (especially the solubility of the obtained dithienylpyrrole oligomers and polymers) and also lead to "cross-linking" at the β-positions of thiophene and pyrrole rings. This gives condensed polyheterocyclic compounds with an extended C=C conjugated system which are promising not only for their electroconductive properties but also as structural fragments of photochromic dihetarylethenes. The aim of this work was a study of several electrophilic substitution reactions of 2,5-di(2-thienyl)pyrroles **1a-c** together with the subsequent reactions of the products obtained.

Vilsmeier formylation of compounds **1a-c** gave high yields (82-97%) of the aldehydes **2a-c**. Rieche type formylation of aldehyde **2b** gave the pyrrole-3,4-dialdehyde **3** (69% based on the aldehyde **2b** taking part in the reaction). The product of a Kishner reduction of aldehyde **2a** is the corresponding methylpyrrole **4** which undergoes Vilsmeier formylation and also Friedel-Crafts acetylation at the sole unsubstituted pyrrole ring position to form aldehyde **5** (90%) and ketone **6** (59%) respectively.

We have also studied the acylation of the N-alkyl-2,5-di(2-thienyl)pyrroles **1a-c** using different reagents. The monoacetyl derivative **7a** was obtained in low yield (10%) by the action of acetyl chloride on compound **1a** in the presence of $SnCl_4$ in benzene for 4 h but significant tarring occurs. Prolonged holding of the same pyrrole **1a** with a mixed anhydride of acetic and trifluoroacetic acids removes the tarring but shows little increase in the yield of the product **7a** (14.6%). Acetylation by dimethylacetamide in the presence of $POCl_3$ was more successful and gave the target ketone **7a** in 47% yield. An excess of acetyl chloride with the dithienylpyrrole **1b** in the presence of $SnCl_4$ for 25 min gave the diacetyl derivative **8a** in 25% yield. Under the

* Dedicated to Boris Aleksandrovich Trofimov on his 70th jubilee.

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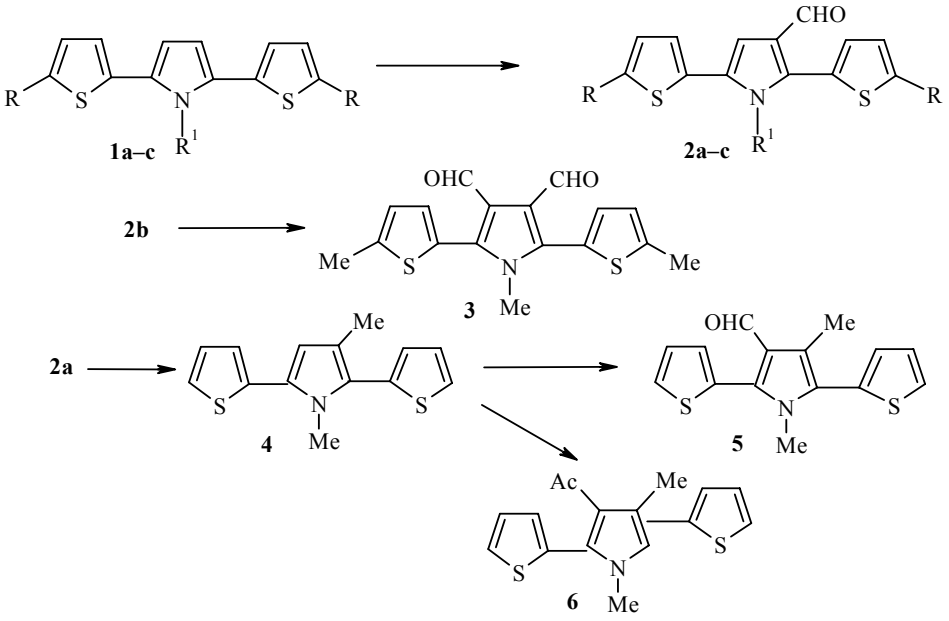
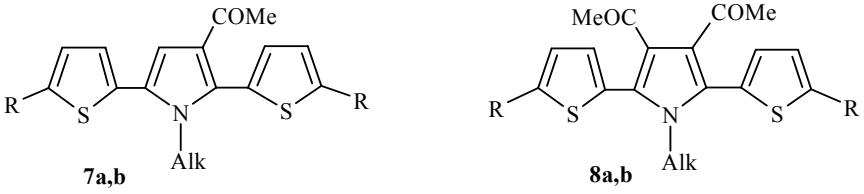


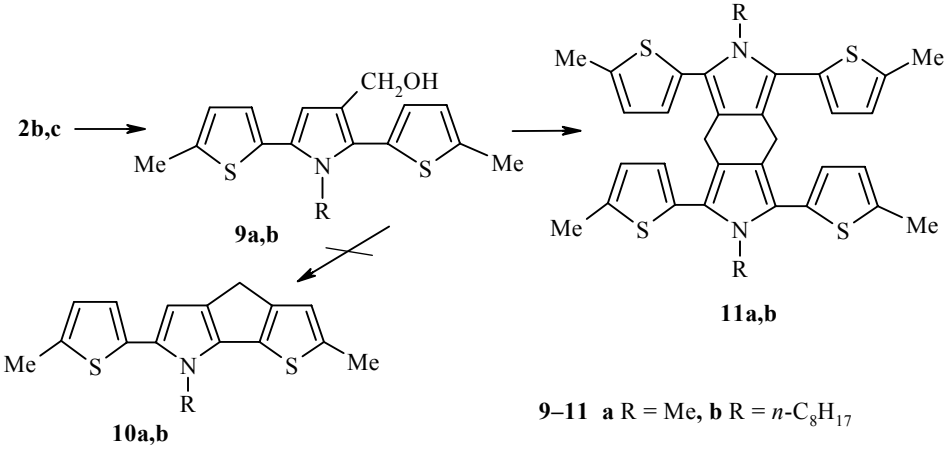
1, 2 **a** R = H, R^1 = Me; **b** R = R^1 = Me; **c** R = Me, R^1 = n-C_8H_{17}

same conditions for 15 min compound **1c** gave only the monoketone **7b** in 22% yield. Increasing this reaction time to 2 h gave a mixture of the monoketone **7b** (19%) and the diketone **8a** (35%) which were separated by column chromatography. The monoketone **7b** was prepared in 48% yield by acetylation of pyrrole **1c** with acetic anhydride in the presence of $SnCl_4$.



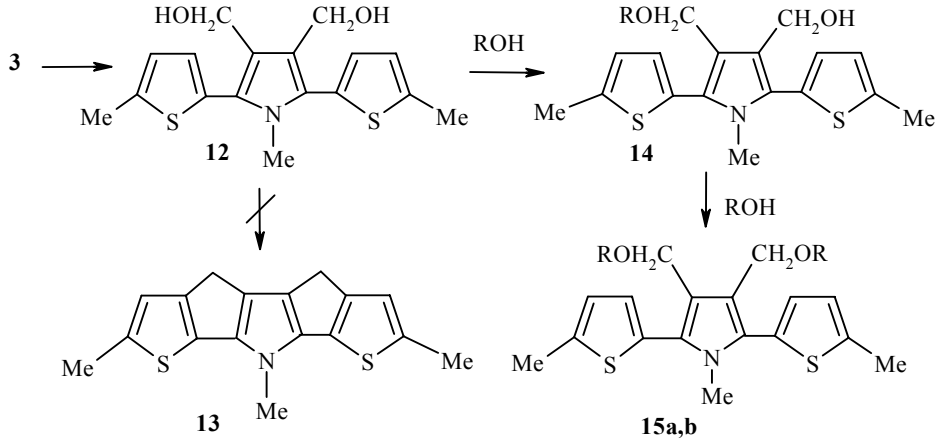
7 a R = H, **b** R = Me; **8 a, b** R = Me; **7**, **8 a** Alk = Me, **b** Alk = n-C_8H_{17}

The reduction of monoaldehydes **2b,c** and dialdehyde **3** were studied using sodium borohydride in methanol or ethanol. It is suggested that the carbinols **9** obtained from monoaldehydes can be converted to the products of an intramolecular alkylation of type **10**. However, it was found that the carbinols **9a,b** (formed in 100 and 51% yields respectively) are quite stable under the reaction conditions but in the presence of HCl undergo intermolecular cyclization with the formation of a six-membered ring giving the compounds **11a,b**.



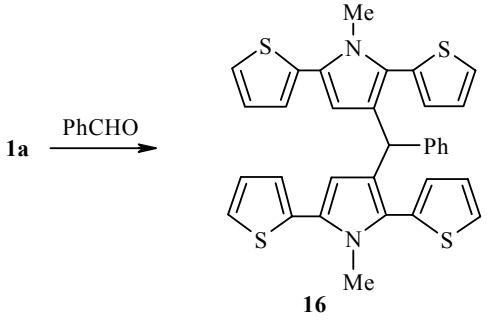
9–11 **a** R = Me, **b** R = n-C_8H_{17}

Since for the biscarbinol **12** (the product of reduction of dialdehyde **3**) a similar intermolecular alkylation is impossible it was thought that the pentacyclic product **13** could be formed as the result of a double intramolecular alkylation. However, compound **12** (prepared in 16% yield) proved stable under borohydride reduction conditions and only partially reacts with methyl or ethyl alcohols in which the reaction was carried out to give the products of O-alkylation **14, 15** respectively.



14, **15a** R = Me, **15b** R = Et

Attempts to carry out hydroxymethylation of **1a,b** catalyzed by HCl and $ZnCl_2$ or "cross-linking a to give the corresponding dihetarylmethanes through the action of paraformaldehyde led only to partial or full tarring. At the same time the action of benzaldehyde on pyrrole **1a** under analogous conditions gave an 87% yield of the dihetarylphenylmethane **16**.



The composition and structure of the products obtained were confirmed by the results of elemental analysis, IR, ^1H and ^{13}C NMR spectroscopic data, and mass spectrometry. Hence we have studied some reactions of 2,5-di(2-thienyl)pyrroles and shown the possibility of optimizing individual reactions to give compounds which may be of interest in the preparation of electroconducting materials and to serve as components of organic light-emitting diodes. Further development based on the obtained polyheterocyclic condensation products can lead to compounds which are promising as the structural fragments of photochromic dihetarylethenes.

EXPERIMENTAL

^1H NMR spectra were taken on Bruker AM-300 (300 MHz), DPX-300 (300 MHz) and AC-200 (200 MHz) radiofrequency spectrometers and on a Bruker DPX-300 (75 MHz) for the ^{13}C NMR spectra and used $CDCl_3$ solvent with the undeuterated residual signal of the solvent as internal standard. EI mass spectra were

taken on a Kratos instrument (70 eV). Monitoring of the course of the reaction was performed on Merck Kieselgel 60 F_{254} plates with petroleum ether–ethyl acetate (2.5:1) as eluent. Preparative separation of the products was performed on columns with Merck SiO_2-60 (0.060-0.200 mm) silica gel with the following solvents or their mixtures as eluents: hexane (HX), diethyl ether (DE), petroleum ether (PE), methylene chloride (MC), or ethyl acetate (EA).

1,4-Di-(2-thienyl)butane-1,4-dione was prepared by the acylation of thiophene with succinic acid dichloride in CH_2Cl_2 in the presence of aluminium chloride using method [7].

1,4-Bis(5-methyl-2-thienyl)butane-2,4-dione was prepared similarly from 2-methylthiophene, mp 170-171°C (EA) (176ºC [8]).

1-Methyl-2,5-bis(2-thienyl)-1H-pyrrole (1a) was synthesized by the reaction of 1,4-di(2-thienyl)-butane-1,4-dione with methylamine in benzene solution in the presence of acetic acid with azeotropic distillation of water [9].

1-Methyl-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole (1b) was prepared similarly from 1,4-bis(5-methyl-2-thienyl)butane-1,4-dione [10].

2,5-Bis(5-methyl-2-thienyl)-1-octyl-1H-pyrrole (1c). A solution of 1,4-bis(5-methyl-2-thienyl)butane-1,4-dione (1 g, 3.6 mmol), N-octylamine (0.51 g, 0.65 ml, 4 mmol) and propionic acid (0.5 ml) in benzene (15 ml) was refluxed in a flask fitted with a Dean and Stark trap for 20.5 h (monitored by TLC). The mixture was cooled, benzene was partially evaporated, and the residue was treated with saturated $NaHCO_3$ solution (5 ml), water (15 ml), and extracted with methylene chloride. The extract was successively washed with water, dilute HCl solution, and water, dried over $MgSO_4$, and evaporated to dryness. Column chromatography (PE) of the residue gave the product **1c** (1.12 g, 84.5%) as a viscous oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.88 (2H, d, *J* ~ 4, H thiophene); 6.73 (2H, d, *J* ~ 4, H thiophene); 6.30 (2H, s, H pyrrole); 4.14 (3H, q, *J* ~ 7, NCH_2); 2.53 (6H, s, 2HetCH_3); 1.20 (2H, m, $NCH_2C\underline{H}_2$); 1.35-1.15 (10H, m, $5CH_2$); 0.92 (3H, t, *J* ~ 7, $CH_2C\underline{H}_3$). Mass spectrum, *m/z*: 278 $[M]^+$. Found, %: C 71.01; H 8.21; S 17.02. $C_{22}H_{29}NS_2$. Calculated, %: C 71.11; H 7.87; S 17.25.

1-Methyl-2,5-di(2-thienyl)-1H-pyrrole-3-carbaldehyde (2a). DMF (0.106 g, 1.454 mmol) was added to a cooled solution (10-12ºC) of $POCl_3$ (0.223 g, 1.454 mmol) in dry CH_2Cl_2 (2 ml), refluxed for 30 min, cooled in an ice bath, and the pyrrole **1a** (0.27 g, 1.1 mmol) was added. The reaction mixture was refluxed with stirring for 1.5 h, cooled, and poured into a solution of $MeCOONa{\cdot}2H_2O$ (1.7 g, 1.454 mmol) in water (10 ml). The emulsion obtained was refluxed for 1 h, cooled, the organic layer separated, and the aqueous layer extracted twice with CH_2Cl_2. The combined extract was washed with a small amount of water, dried over $MgSO_4$, filtered, evaporated on a rotary evaporator to dryness, and the residue was then triturated in a small volume of hexane. The precipitated crystals of product **2a** were filtered off and dried. Yield 0.217 g (90.5%); mp 110-112ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.70 (1H, s, CH=O); 7.56 (1H, dd, ^3J = 4.2, ^4J = 2.2, H thiophene); 7.38 (1H, dd, ^3J = 5.0, ^4J = 1.2, H thiophene); 7.20 (2H, m, H thiophene); 7.13 (2H, m, H thiophene); 6.92 (1H, s, H-4 pyrrole); 3.63 (3H, s, NCH_3). ^{13}C NMR spectrum, δ, ppm: 33.29 (NCH_3); 108.9 (C-4 pyrrole); 126.29, 126.99, 127.49, 128.68, 130.82; 186.01 (CH=O). Found, %: C 61.49; H 4.3; N 5.14. $C_{14}H_{11}NOS_2$. Calculated, %: C 61.51; H 4.06; N 5.12.

1-Methyl-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole-3-carbaldehyde (2b) is prepared similarly to aldehyde **2a** from pyrrole **1b** (0.45 g, 1.65 mmol), $POCl_3$ (0.334 g, 2.1 mmol), and DMF (0.154 g, 2.1 mmol) in dry CH_2Cl_2 (2 ml) with silica gel column purification (PE-EA, 10:1). Yield 0.48 g (96.7%); mp 90ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.70 (1H, s, CHO); 6.92 (1H, d, *J* ~ 4, H thiophene); 6.87 (1H, d, *J* ~ 4, H thiophene); 6.80 (1H, br. s, H thiophene); 6.73 (1H, s, H-4 pyrrole); 6.71 (1H, br. s, H thiophene); 3.60 (3H, s, NCH_3); 2.55 (3H, s, CCH_3); 2.50 (3H, s, CCH_3). Found, %: C 63.78; H 5.00; N 4.67; S 20.81. $C_{16}H_{15}NOS_2$. Calculated, %: C 63.76; H 5.02; N 4.65; S 21.27.

2,5-Bis(5-methyl-2-thienyl)-1-octyl-1H-pyrrole-3-carbaldehyde (2c) is prepared and purified similarly to aldehyde **2b** from pyrrole **1c** (0.33 g, 0.083 mmol), $POCl_3$ (0.19 g, 1.2 mmol), and DMF (0.09 g,

1.2 mmol) in dry CH_2Cl_2 (7 ml). Yield 0.29 g (82%) as a viscous oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.63 (1H, s, CHO); 6.95 (1H, br. s, H thiophene); 6.90 (1H, br. s, H thiophene); 6.80 (1H, br. s, H thiophene); 6.76 (1H, s, H-4 pyrrole); 6.71 (1H, br. s, H thiophene); 4.00 (2H, t, $J \sim 7$, NCH_2); 2.55 (3H, s, CCH_3); 2.50 (3H, s, CCH_3); 1.50-1.10 (12H, m, $6CH_2$); 0.85 (3H, t, $J \sim 7$, $CH_2C\underline{H}_3$). Found, %: C 69.48; H 7.38; N 3.47; S 15.80. $C_{23}H_{29}NOS_2$. Calculated, %: C 69.13; H 7.31; N 5.50; S 16.05.

1-Methyl-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole-3,4-dicarbaldehyde (3). Aldehyde **2b** (0.3 g, 1.0 mmol) in CH_2Cl_2 (3 ml) and a solution of Cl_2CHOEt (prepared from PCl_5 (0.315 g, 1.5 mmol) and ethyl formate (0.125 g, 1.69 mmol) in dry CH_2Cl_2 (3 ml)) were added simultaneously with stirring and cooling (10-12ºC) to a solution of $TiCl_4$ (0.663 g, 3.5 mmol) in dry CH_2Cl_2 (1.5 ml). The mixture was held for 35 min at 10-12ºC, poured into ice with HCl, and the product was stirred for 20 min. The aqueous layer was separated and extracted with CH_2Cl_2 and the combined extract was washed with water, dried over $MgSO_4$, and filtered. Evaporation to dryness gave a residue (0.4 g) which was column chromatographed (PE–EA, 10:1) to give the aldehyde **2b** (0.1 g) and dialdehyde **3** (0.15 g, 45.7% as taken or 68.5% based on the **2b** taking part in the reaction). Recrystallization from hexane gave an analytically pure sample of product **3** with mp 132ºC. ^{1}H NMR spectrum, δ, ppm; 10.15 (2H, s, 2CHO); 7.02 (2H, br. s, H thiophene); 6.85 (2H, br. s, H thiophene); 3.47 (3H, s, NCH_3); 2.55 (6H, s, CCH_3). Found, %: C 61.96; H 4.56; N 4.21; S 19.59. $C_{17}H_{15}NO_2S_2$. Calculated, %: C 61.98; H 4.59; N 4.25; S 19.46.

1,3-Dimethyl-2,5-di(2-thienyl)-1H-pyrrole (4). A solution of aldehyde **2a** (0.2 g, 0.7316 mmol), hydrazine hydrate (0.071 g, 2.21 mmol) and KOH (0.2 g, 3.57 mmol) in triethylene glycol (40 ml) was held for 3 h at 200-240ºC, then for 1 h at 190-200ºC, and cooled. The reaction mixture was diluted with water (50 ml), extracted three times with benzene, and the combined extract was washed twice with water, dried over $CaCl_2$, filtered, and evaporated. Flash chromatography of the residue (EA–HX, 1; 10) gave the product **4** (0.178 g, 93.8%) as a yellow oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.40 (1H, dd, $^3J = 5.0$, $^4J = 1.2$, H-5 thiophene); 7.27 (1H, dd, $^3J = 5.0$, $^4J = 1.5$), H-5' thiophene); 7.13 (1H, dd, $^3J = 5.2$, $^3J = 3.5$, H-4 thiophene); 7.05 (3H, m, H-4' thiophene); 6.27 (1H, d, $J = 0.4$, H pyrrole); 3.60 (3H, s, NCH_3); 2.13 (1H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 13.32 (CH_3); 34.81 (NCH_3); 112.2 (C-4 pyrrole); 120.81 (C-3 pyrrole); 126.06, 126.57, 126.99, 127.53, 128.43, 128.71, 129.09, 129.49, 134.98, 136.45. Found, %: C 64.93; H 5.15; N 5.91. $C_{14}H_{13}NS_2$. Calculated, %: C 64.82; H 5.05; N 5.40.

1,4-Dimethyl-2,5-di(2-thienyl)-1H-pyrrole-3-carbaldehyde (5). DMF (0.106 g, 1.45 mmol) was added to a cooled solution of $POCl_3$ (0.223 g, 1.45 mmol) in dry CH_2Cl_2 (2 ml) and the mixture was refluxed for 30 min, cooled in an ice bath, and the pyrrole **4** (0.270 g, 1.1 mmol) was added. The reaction mixture was refluxed with stirring for 90 min, cooled, and poured into a solution of $MeCOONa{\cdot}2H_2O$ (1.7 g, 1.454 mmol) in water (10 ml). The emulsion obtained was refluxed for 1 h, cooled, the organic layer separated, and the aqueous layer extracted twice with CH_2Cl_2. The combined extract was washed with a small amount of water, dried over $MgSO_4$, filtered, evaporated to dryness on a rotary evaporator, and the residue was triturated in a small volume of hexane. The precipitated crystals were filtered off and dried to give the product **5** (0.217 g, 90.5%). Mp 128-130ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 9.75 (1H, s, CH=O); 7.54 (1H, dd, $^3J = 4.2$, $^4J = 2.2$, H thiophene); 7.47 (1H, dd, $^3J = 5.2$, $^4J = 1.2$, H thiophene); 7.17 (3H, m, H thiophene); 7.06 (1H, dd, $^3J = 3.5$, $^4J = 1.2$, H thiophene); 3.44 (3H, s, NCH_3); 2.33 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 11.94 ($C\underline{C}H_3$ pyrrole); 33.74 (NCH_3); 121.58, 123.76, 128.02, 128.12, 128.22, 129.20, 130.33, 131.61, 131.84, 188.07 (CH=O). Found, %: C 62.80; H 4.56; N 4.88. $C_{15}H_{13}NOS_2$. Calculated, %: C 62.69; H 4.56; N 4.87.

3-Acetyl-1,4-dimethyl-2,5-di(2-thienyl)-1H-pyrrole (6). A solution of $SnCl_4$ (0.042 g, 0.69 mmol) in dry benzene (1 ml) was added to a cooled solution of acetic anhydride (0.071 g, 0.696 mmol) and pyrrole **4** (0.158 g, 0.6091 mmol) in dry benzene (30 ml). The reaction mixture was stirred for 4 h at room temperature, poured into an iced solution of conc. HCl (1 ml) in water (50 ml), and the mixture was vigorously shaken in a separating funnel. The organic layer was separated and the aqueous layer was extracted three times with benzene. The combined extract was washed with a strongly dilute solution of HCl, water, and $NaHCO_3$

solution, dried over $CaCl_2$, and then evaporated in a rotary evaporator. Column chromatography of the residue (EA–HX, 1:10) gave the starting compound **4** (0.042 g, 26.5%) and ketone **6** (0.109 g, 59.2%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.53 (1H, dd, ^3J = 5.1, ^4J = 1.2, H-5 thiophene); 7.45 (1H, dd, ^3J = 5.1, ^4J = 1.2, H-5' thiophene); 7.13 (3H, m, thiophene); 7.04 (1H, dd, ^3J = 3.5, ^4J = 1.1, H-4 thiophene); 3.29 (3H, s, NCH_3); 2.26 (3H, s, $COC\underline{H}_3$); 2.01 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 12.61 (CH_3); 30.36 ($CO\underline{C}H_3$); 33.30 (NCH_3); 122.16 (C-4 pyrrole); 125.30 (C-3 pyrrole); 126.31, 127.65, 127.78, 127.91, 129.08, 129.99, 130.51, 131.09, 132.24 133.10; 196.46 ($\underline{C}OCH_3$); Found, %: C 63.41; H 5.22; N 4.62. $C_{16}H_{15}NOS_2$. Calculated, %: C 63.76; H 5.02; N 4.65.

3-Acetyl-1-methyl-2,5-di(2-thienyl)-1H-pyrrole (7a). A. From AcCl (0.055 g, 0.70 mmol) and pyrrole **1a** (0.165 g, 0.71 mmol) (in 5 ml dry benzene) and $SnCl_4$ (0.182 g, 0.69 mmol) in (1 ml dry benzene) using the method of synthesis of compound **6**. Chromatography (EA–HX, 1:8) of the combined extract after evaporation of the solution dried over $MgSO_4$ gave ketone **7a**, (0.0196 g, 10.1%), mp 124-125ºC (alcohol) ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.54 (1H, dd, ^3J = 4.9, ^4J = 1.2, H-5 thiophene); 7.45 (1H, dd, ^3J = 5.2, ^4J = 1.1, H-5' thiophene); 7.17 (2H, m, H thiophene); 7.10 (2H, m, H thiophene); 6.84 (1H, s, H pyrrole); 3.48 (3H, s, NCH_3); 2.15 (3H, s, $COCH_3$). ^{13}C NMR spectrum, δ, ppm: 27.4 ($CO\underline{C}H_3$); 32.07 (NCH_3); 110.11 (C-4 pyrrole); 124.93, 125.63, 126.27, 126.41, 127.48, 129.55, 130.97, 192.67 ($\underline{C}OCH_3$). Found, %: C 62.74; H 4.58; N 4.64. $C_{15}H_{13}NOS_2$. Calculated, %: C 62.69; H 4.56; N 4.87.

B. A solution of acetic anhydride (0.168 g, 1.64 mmol), CF_3COOH (0.414, 3.6 mmol) and pyrrole **1a** (0.134 g, 0.548 mmol) in dry CH_2Cl_2 (4 ml) was stirred for 15 h, poured into a saturated solution of $NaHCO_3$, stirred for 20 min, and the aqueous layer was separated and extracted three times with CH_2Cl_2. The combined extract was washed with water, then $NaHCO_3$ solution, dried over $MgSO_4$, and evaporated. Column chromatography of the residue (HX–MC–EA, 14:4:1) gave ketone **7a** (0.023 g, 14.6%).

C. N,N-Dimethylacetamide (1 ml) was added to $POCl_3$ (1 ml) with cooling in an ice bath and the mixture obtained was held on a refluxing water bath for 1 h, cooled to 0ºC, and pyrrole **1a** (0.2 g, 0.815 mmol) was added. The reaction mixture was held on a boiling water bath for 3 h, cooled, poured into a solution of $AcONa{\cdot}2H_2O$ (15 g) in water (75 ml), CH_2Cl_2 (10 ml) added, and refluxed with vigorous stirring for 1 h. After cooling the organic layer was separated and the aqueous layer was extracted three times with CH_2Cl_2. The combined extract was washed twice with water, then $NaHCO_3$ solution and a solution of $CaCl_2$, dried over Na_2SO_4, and evaporated. Column chromatography of the residue (EA–HX, 1:8) gave the product **7a** (0.11 g, 47%).

Samples of ketone **7a** prepared by methods A-C were identical by TLC.

3,4-Diacetyl-1-methyl-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole (8a). $SnCl_4$ (0.191 g, 0.733 mmol) in benzene (4 ml) was added dropwise to a mixture of compound **1b** (0.2 g, 0.733 mmol) and acetyl chloride (0.12 g, 1.47 mmol) at a temperature not exceeding 5ºC. The dark-red solution formed was held for 25 min and poured onto ice in the presence of HCl. The aqueous layer was separated and extracted twice with chloroform and the combined extract was washed with water and dried over $MgSO_4$. Evaporation of solvent gave a residue (0.28 g) from which column chromatography (PE–EA, 10:1 and then 5:1) gave the product **8a** (0.06 g, 25%); mp 138ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.92 (2H, br. s, H thiophene); 6.78 (2H, d, *J* ~ 4, H thiophene); 3.32 (3H, s, NCH_3); 2.52 (6H, s, $2CCH_3$); 2.20 (6H, s, $2COCH_3$). Found, %: C 63.99; H 5.29; N 4.05. $C_{19}H_{19}NO_2S_2$. Calculated, %: C 63.84; H 5.36; N 3.92.

3-Acetyl-2,5-bis(5-methyl-2-thienyl)-1-octyl-1H-pyrrole (7b) and **3,4-Diacetyl-2,5-bis(5-methyl-2-thienyl)-1-octyl-1H-pyrrole (8b)** A. Acetyl chloride (0.085 g, 1.08 mmol) and then $SnCl_4$ (1 drop) in benzene (0.5 ml) was added to a solution of compound **1c** (0.2 g, 0.54 mmol) in dry benzene (3.5 ml) at 10°C. The dark-red solution formed was held for 15 min and poured onto ice in the presence of HCl. After 15 min the light organic layer was separated, the aqueous layer extracted twice with chloroform, and the combined extract washed with water and dried over $MgSO_4$. Evaporation of solvent gave an oily residue (0.28 g) from which column chromatography (PE–EA, 10:1) gave the starting **1c** (0.15 g, 75%) and the product **7b** (0.05 g, 22%) as an oil.

^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.91 (1H, d, *J* ~ 4, H thiophene); 6.88 (1H, d, *J* ~ 4, H thiophene); 6.78 (1H, d, *J* ~ 4, H thiophene); 6.75 (1H, s, H pyrrole); 6.72 (1H, d, *J* ~ 4, H thiophene); 3.88 (2H, t, *J* ~ 7, NCH_2); 2.57 (3H, s, CCH_3); 2.52 (3H, s, CCH_3); 2.16 (3H, s, CH_3CO); 1.60-1.10 (12H, m, $6CH_2$); 0.88 (3H, t, *J* ~ 7, $CH_2C\underline{H}_3$). Found, %: C 71.20; H 7.60; S 15.22. $C_{24}H_{31}NOS_2$. Calculated, %: C 69.69; H 7.55; S 15.50.

B. As in the above method but holding the reaction mixture for 2 h gave the starting **1c** (0.014 g, 7%), the monoacylation product **7b** (0.043 g, 19%), and the diacylation product **8b** (0.086 g, 35%) as an oil. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.92 (2H, d, *J* ~ 4, H thiophene); 6.78 (2H, d, *J* ~ 4, H thiophene); 3.76 (2H, t, *J* ~ 7, NCH_2); 2.55 (6H, s, $2CCH_3$); 2.16 (6H, s, $2CH_3CO$); 1.60-1.00 (12H, d, $6CH_2$); 0.88 (3H, t, *J* ~ 7, $CH_2C\underline{H}_3$). Found, %: C 68.40; H 7.58; S 13.52. $C_{26}H_{33}NO_2S_2$. Calculated, %: C 68.53; H 7.30; S 14.07.

C. Acetic anhydride (0.05 g, 0.5 mmol) was added to a solution of compound **1c** (0.15 g, 0.4 mmol) in dry benzene (20 ml) at 10ºC followed by dropwise addition of a solution of $SnCl_4$ (0.027 g, 0.45 mmol) in benzene (1 ml). The dark-violet solution formed was held for 3 h at room temperature and poured into iced water. When shaken the mixture took on a light-lilac color. The organic layer was separated, washed with dilute HCl and water, and dried over $MgSO_4$. Evaporation of the solvent gave an oil (0.2 g), column chromatography of which (PE–EA, 10:1) gave the starting **1c** (0.04 g, 27%) and the product **7b** (0.08 g, 48%), identical to the sample prepared as in method A by TLC.

3-Hydroxymethyl-1-methyl-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole (9a). A solution of $NaBH_4$ (0.1 g, 2.66 mmol) in absolute ethanol (1.5 ml) was added at ~ 20ºC to a suspension of aldehyde **2b** (0.2 g, 0.66 mmol) in methanol (3.5 ml). After 15 min a solution was formed which was held for 2 h at room temperature, water (1.5 ml) saturated with potassium carbonate was added, and the product was extracted with ether. Evaporation of solvent gave ~ 0.2 g of white, crystalline product **9a** (quantitative yield) with mp 88-91ºC, stable upon storage, which was then washed with hexane to give an analytically pure sample with mp 95ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.88 (1H, *J* ~ 4, H thiophene); 6.85 (1H, d, *J* ~ 4, H thiophene); 6.80 (1H, br. s, H thiophene); 6.73 (1H, br. s, H thiophene); 6.39 (1H, s, H pyrrole); 4.52 (2H, br. s, CH_2); 3.60 (3H, s, NCH_3); 2.55 (3H, s, CCH_3); 2.53 (3H, s, CCH_3); the OH signal was not observed because of exchange with water present in the $CDCl_3$. Mass spectrum, *m/z* (I_{rel}, %): 303 $[M]^+$ (100), 286 $[M\text{-}OH]^+$ (30). Found, %: C 63.55; H 5.87; N 4.60. $C_{16}H_{17}NOS_2$. Calculated, %: C 63.32; H 5.65; N 4.63.

2,6-Dimethyl-1,3,5,7-tetrakis(5-methyl-2-thienyl)-4,8-dihydropyrrolo[3,4-*e*]benzo[*b*]pyrrole (11a). Upon keeping a solution of carbinol **9a** in chloroform or methylene chloride containing traces of HCl it was gradually converted to compound **11a** with mp 240-250ºC. An analytically pure sample formed after column purification (PE–EA, 10:1) has mp 255ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.62 (4H, br. s, H thiophene); 6.48 (4H, d, *J* ~ 4, H thiophene); 3.68 (4H, s, $2CH_2$); 3.31 (6H, s, $2NCH_3$); 2.49 (12H, s, $4CCH_3$). Mass spectrum, *m/z* (I_{rel}, %): 570 $[M]^+$ (100), 303 (72). Found, %: C 67.43; H 5.43; N 4.56. $C_{32}H_{30}N_2S_4$. Calculated, %: C 67.32; H 5.30; N 4.93.

3-Hydroxymethyl-2,5-bis(5-methyl-2-thienyl)-1-octyl-1H-pyrrole (9b) and **1,3,5,7-Tetrakis(5-methyl-2-thienyl)-2,6-dioctyl-4,8-dihydropyrrolo[3,4-*e*]benzo[*b*]pyrrole (11b)**. A suspension of aldehyde **2c** (0.29 g, 0.73 mmol) in a solution of $NaBH_4$ (0.125 g, 3.32 mmol) in MeOH (7 ml) was stirred for 3 h at a temperature not exceeding 20ºC. A saturated solution of K_2CO_3 (1.5 ml) was added to the solution formed which was then extracted with ether. The extract was dried, evaporated, and the residue was column chromatographed (PE–EA, 20:1) to give the products **11b** (0.08 g, 27%) and **9b** (0.17 g, 51%), both in the form of an oil.

Compound 11b. Mass spectrum, *m/z* (I_{rel}, %): 653 $[M\text{–}C_8H_{17}]^+$ (56), 540 $[M\text{–}C_8H_{17}\text{–}C_8H_{17}]^+$ (21), 384 $[M/2+H]^+$ (36), 149 (75), 59 (100). Found, %: C 71.35; H 7.85; N 3.31. $C_{46}H_{30}N_2S_4$. Calculated, %: C 72.01; H 7.62; N 3.65.

Compound 9b. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.86 (1H, d, *J* ~ 4, H thiophene); 6.85 (1H, d, *J* ~ 4, H thiophene); 6.78 (1H, d, *J* ~ 4, H thiophene); 6.73 (1H, d, *J* ~ 4, H thiophene); 6.40 (1H, s, H pyrrole); 4.50 (2H, br. s, OCH_2); 4.00 (2H, t, *J* ~ 7, NCH_2); 2.55 (3H, s, CCH_3); 2.52 (3H, s, CCH_3); 1.50-1.10 (12H, m, $6CH_2$); 0.88 (3H, t, *J* ~ 7, CH_3). The OH signal was not observed due to exchange with water present in $CDCl_3$.

Mass spectrum, *m/z* (I_{rel}, %): 401 $[M]^+$ (100), 385 (44), 288 (13), 272 (31), 258 (29). Found, %: C 69.61; H 7.48; N 3.37. $C_{23}H_{31}NOS_2$. Calculated, %: C 68.78; H 7.78; N 3.49.

3,4-Bis(hydroxymethyl)-1-methyl-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole (12), 3-Hydroxymethyl-1-methyl-4-methoxymethyl-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole (14), and **1-Methyl-3,4-bis(methoxymethyl)-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole (15a)**. A solution of $NaBH_4$ (0.034 g, 0.91 mmol) in absolute methanol (0.7 ml) was added at a temperature not exceeding 20ºC to a suspension of the dialdehyde **3** (0.06 g, 0.182 mmol) in methanol (1 ml). The obtained mixture was held for 2 h at room temperature, water saturated with K_2CO_3 (1.5 ml), was added, and it was extracted with ether. Column chromatography (PE–EA, 10:1) of the residue after evaporation of the extract gave two fractions of 0.02 g (both of them were viscous oils). The first contained the product **15a**. Mass spectrum, *m/z* (I_{rel}, %): 361 $[M]^+$ (42), 301 (100). The second fraction contained the product **14**. Mass spectrum, *m/z* (I_{rel}, %): 347 $[M]^+$ (59), 316 (58), 301 (36), 285 (40), 57 (100). Elution of the column with DE then gave the product **12** (0.01 g, 16%) which was washed with hot hexane to give a sample for analysis with mp 145-146ºC. ^{1}H NMR spectrum, δ, ppm: 6.88 (2H, br. s, H thiophene); 6.79 (2H, br. s, H thiophene); 4.60 (4H, s, $2CH_3$); 3.47 (3H, s, NCH_3); 2.53 (6H, s, $2CCH_3$): the OH signal is not observed due to exchange with water present in $CDCl_3$. Mass spectrum, *m/z* (I_{rel}, %): 333 $[M]^+$ (100), 315 $[M–H_2O]^+$ (41), 256 (86), 140 (84). Found, %: C 61.01; H 5.76; N 4.32; S 18.46. $C_{17}H_{19}NO_2S_2$. Calculated, %: C 61.23; H 5.74; N 4.20; S 19.23.

Reduction of the dialdehyde **3** (0.06 g, 0.182 mmol) using $NaBH_4$ (0.05 g, 1.34 mmol) in MeOH (2.5 ml) (~ 20ºC, 1 h and subsequent treatment of the mixture with 1 ml of saturated aqueous potassium carbonate solution) gave the product **12** in 85% yield with mp 125ºC (without purification), identical to the sample described above (TLC, HX–EA, 2.5:1).

3,4-Bis(ethoxymethyl)-1-methyl-2,5-bis(5-methyl-2-thienyl)-1H-pyrrole (15b). A solution of $NaBH_4$ (0.056 g, 1.5 mmol) in absolute methanol (0.7 ml) was added to a suspension of the dialdehyde **3** (0.1 g, 0.3 mmol) in ethanol (3 ml) with cooling (≤ 20ºC). The mixture was held for 1.5 h at ~ 20ºC, water saturated with potassium carbonate (1 ml) was added, and the product extracted with ether. The extract was washed with water, dried over $MgSO_4$, and evaporated to give an oily residue (0.065 g) containing a mixture of three compounds (TLC, HX–EA, 2.5:1). Extraction with hexane and subsequent column chromatography (PE–EA, 10:1) of the extract gave the product **15b** (0.025 g, 21%). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.90 (2H, br. s, H thiophene); 6.76 (2H, br. s, H thiophene); 4.42 (4H, s, $2CH_2$); 3.53 (4H, q, *J* ~ 7, $2C\underline{H}_2CH_3$); 3.45 (3H, s, NCH_3); 2.55 (6H, s, $2CCH_3$); 1.22 (6H, t, *J* ~ 7, $2CH_2C\underline{H}_3$). Mass spectrum, *m/z* (I_{rel}, %): 389 $[M]^+$ (45), 314 (30), 300 (100), 286 (39).

Bis[1-methyl-2,5-(2-thienyl)-1H-pyrrol-3-yl]phenylmethane (16). A mixture of benzaldehyde (0.105 g, 0.95 mmol) and di(2-thienyl)-1H-pyrrole **1a** (0.25 g, 0.102 mmol) in ethanol (50 ml) was refluxed in the presence of a catalytic amount of a 30% solution of HCl (1-2 drops) and $ZnCl_2$ (1 small crystal) over 14 h. The product was cooled and the precipitated crystals were filtered off, dried, and purified by flash chromatography (EA–HX, 8:1) to give pale-green crystals of product **16** (0.257 g, 87%) with mp 154-156ºC. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 7.30 (2H, dd, ^3J = 5.2, ^4J = 1.1, H-5 thiophene); 7.12 (1H, m, *p*-H phenyl); 7.05 (4H, m, H phenyl); 6.94 (2H, dd, ^3J = 3.5, ^3J = 5.2, H-4 thiophene); 6.70 (2H, dd, ^3J = 3.5, ^4J = 1.1, H-3 thiophene); 6.36 (2H, s, H pyrrole); 5.22 (1H, s, $C\underline{H}C_6H_5$); 3.57 (6H, s, 2 NCH_3). ^{13}C NMR spectrum, δ, ppm: 34.11 (NCH_3); 40.67 ($Het_2Ph\underline{C}$); 111.10 (C-4 pyrrole); 125.20, 125.89, 126.07, 127.17, 127.41, 127.93, 128.40, 128.58, 128.77, 129.02, 129.57, 133.59, 135.98, 147.06 (*p*-C phenyl). Found, %: C 67.78; H 4.96; N 4.75. $C_{33}H_{26}N_2S_4$. Calculated, %: C 68.47; H 4.53; N 4.84.

This work was carried out with the support of the Presidium of the Russian Academy of Sciences (Program. No. 8, "Study of methods for preparing chemical substances and development of novel materials").

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